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Volume II. Appendixes

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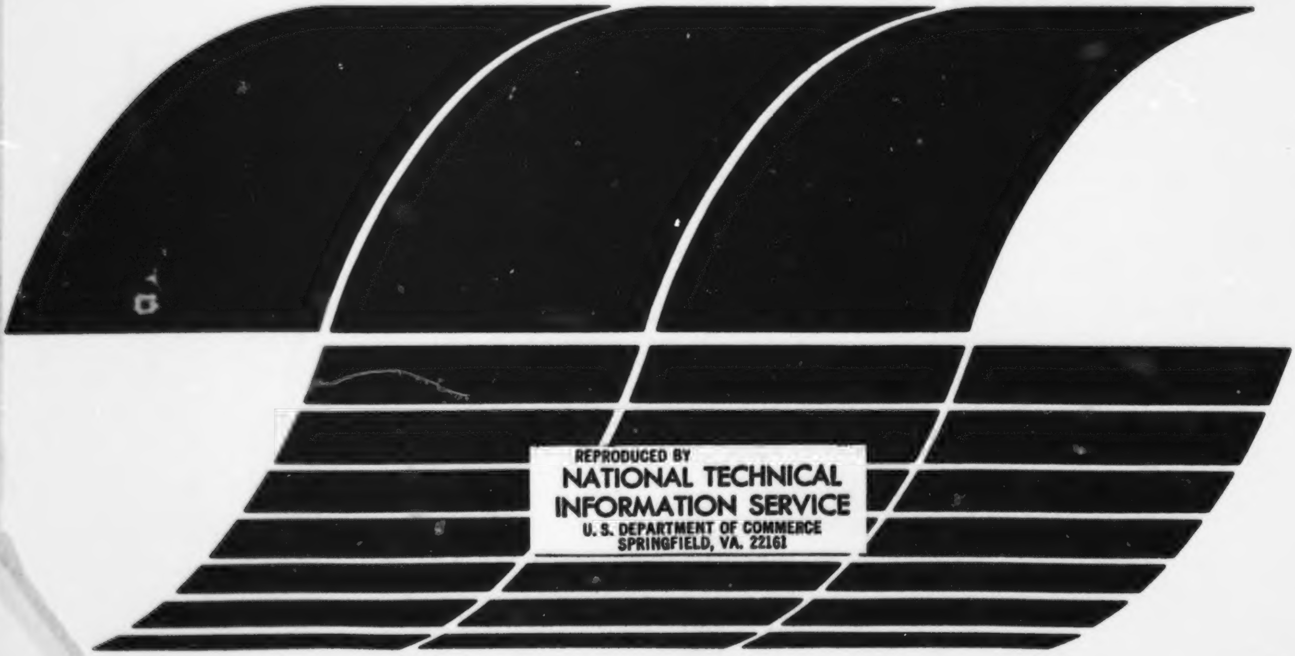

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16. ABSTRACT

The report gives results of an investigation of water recycle/treatment/reuse alternatives in coal-fired power plants. Five power plants from representative U.S. regions were studied. The major water systems encountered were cooling, ash sluicing, and SO2/particulate scrubbers. Results were used to provide general implementation plans for the various options identified. Computer models were used to identify the degree of recirculation achievable in each water system without forming scale. The effects of makeup water quality and various operating parameters were determined for each water system. Several alternatives for minimizing water requirements and discharges were studied for each plant, and rough cost estimates were made for comparison. An implementation plan is presented for each water system and is divided into phases, including system characterization, alternative evaluation, pilot studies, and full-scale implementation. This volume presents detailed studies for each plant, plant selection methodology, laboratory ash sluicing studies, kinetics for CaCO3 and Mg(OH)2 precipitation, and model descriptions.

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Volume II. Appendixes

by

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ABSTRACT

This study was conducted under EPA Contract No. 68-03-2339 to investigate water recycle/reuse alternatives in coal-fired power plants. In the first part of this program, five typical plants from representative geographical regions of the United States were studied. The major types of water systems encountered at these plants were cooling towers, ash sluicing, and SO_2/particulate scrubbing.

Computer models were used to identify the degree of recirculation achievable in each of these water systems without forming scale. The effects of makeup water quality and various operating parameters were determined for each water system using the models. Several alternatives for minimizing water requirements and discharges were studied for each plant and rough cost estimates were made to compare alternatives.

In the second part of the program generalized implementation plans for the options identified in the plant studies are presented. An implementation plan is presented for each major water system (cooling towers, ash sluicing, scrubbing) where the plans are divided into phases. The phases include system characterization, alternative evaluation, pilot studies, and full-scale implementation. The characterization phase for each system includes discussions of the important process variables to consider when modifying the system. The alternative evaluation phase descriptions include discussions of various recycle/reuse alternatives and present methodologies for evaluating the feasibility of those options. The pilot studies and full-scale implementation discussions include descriptions of equipment required and important operating variables to be considered.

The overall report is presented in two volumes. The first volume discusses the recycle/reuse opportunities for cooling tower, ash sluicing, and SO_2/particulate scrubbing systems, as well as for combined systems. The first volume also contains the results of the studies to prepare generalized implementation plans. Volume II presents the detailed studies for each plant, the selection methodology, the results of the laboratory studies for ash sluicing, the results of kinetic studies for $CaCO_3$ and $Mg(OH)_2$, and a description of the models used in this study.

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APPENDIX A

POWER PLANT SELECTION CRITERIA

1.0 INTRODUCTION

In order to meet the national goal of "zero-discharge" of pollutants to the environment, steam-electric power plants must consider all possibilities for recycle and reuse of wastewater streams. This situation is enhanced by limited availability and rising costs of water along with water treatment requirements.

This project involved studying the water streams and possible recycle/reuse alternatives at five typical steam-electric power plants in the United States. This appendix describes the selection of the typical plants studied.

First, the criteria used in selecting the plant sites are discussed. These include geographical location, power plant cooperation and data availability, site characteristics, and project timing. Next, the selection of the plants in each area is discussed. Steam-electric power plants in each geographical region are identified and discussed with respect to the criteria outlined above. General data for the final plant sites selected for study are then assembled and inspected to insure that a general spectrum of cooling systems, ash handling systems, and pollution control equipment is included.

2.0 SELECTION CRITERIA

Representative site selection necessitates establishing criteria pertinent to the overall objectives of the program. The four main criteria selected for screening the steam-electric power plants are:

1) location,
2) availability,
3) site characteristics, and
4) timing.

The first criterion, location, represents the geographical area in which the plant is located. Four geographical regions were initially defined: Southwest, Northern Great Plains, Northeast, and Southeast. These four areas were chosen to represent regions in the United States where water recycle/reuse is advantageous due to high water costs, limited water availability, or wastewater treatment and disposal problems. By selecting plants located in these geographical areas of the United States, different types of cooling modes will be examined. The different climatological conditions associated with each geographical region determine to some extent the type of cooling and/or waste disposal methods. For example, cooling ponds and evaporation ponds are most suitable for hot, dry climates such as found in the Southwest than the more humid climates of the Southeast.

The second criterion listed is availability. This involves both data accessibility and plant cooperation. Sufficient plant water data will be necessary to confirm information gathered from sampling. This will insure an accurate characterization of each plant's water system and serve as confirmation of the validity of the process simulation model.

Power plant cooperation is an extremely important factor in selecting typical sites for study. A good working relationship is essential to the successful completion of the project. Also, the possible implementation of a demonstration program following the existing work will depend upon the plant's cooperation.

Site characteristics, the third criterion, consist of the plant cooling, ash handling, and pollution control systems. Three types of cooling systems may be employed by a power plant: once-through cooling, cooling towers, or cooling ponds. Plants with cooling towers or cooling ponds are preferred since these types of cooling systems are good candidates for recycle/reuse options whereas once-through systems are not. Wet ash sluicing is similarly preferred over dry handling for the purposes of this study.

The pollution control systems of the plants studied are also taken into account in selecting the plants. The type of particulate control utilized may play a significant role in the water management scheme of the plant. For instance, make-up water for particulate or SO_2 scrubbers may be provided by wastewater streams which are normally discharged.

The last criterion, timing, concerns the status of studies or plant modifications which are planned or underway. Plants which are conducting studies involving the water system may be able to supply more accurate data which is pertinent to this study. Plants which are planning modifications such as the installation of SO_2 scrubbers may have additional recycle/reuse options that can be studied.

The aforementioned criteria were used to examine the potential plants identified in each geographical area. The following section contains a discussion of these plants and presents the data collected in tabular form.

3.0 SELECTION METHODOLOGY

This section describes the methodology used to select the plants to be studied in the water management program. First, potential power plants are identified in each region based on data concerning the plants' cooling, ash handling, particulate control and sulfur dioxide control systems. Then the potential plants identified are screened on the basis of the selection criteria discussed in the previous section. The final selection of the plants to be studied involved contacting each of the utilities to determine their interest in the program. Five plants (Arizona Public Service's Four Corners Plant, Public Service of Colorado's Comanche Plant, Georgia Power's Bowen Plant, Pennsylvania Power and Light's Montour Plant, and Montana Power's Colstrip Plant) were selected for the study.

3.1 Plant Identification

Identification of potential power plants in each geographical region was accomplished by assembling published data concerning coal-fired steam-electric power plants for the Southwest, Northern Great Plains, Southeast, and the Northeast regions of the United States. This section presents and describes the data collected for the potential plants identified in each geographical area. The data concerning location, capacity, and the types of cooling, ash handling, particulate control and sulfur dioxide control systems is presented in tabular form for each region.

3.1.1 Southwest

The potential power plants for the water management program in the Southwest are presented in Table 3-1. Two of the seven plants shown were included in a list of recommended study sites for the project that was sent to EPA-NERL (Thermal Pollution Branch) from the EPA Office of Energy Activities in Denver, Colorado. These two plants are Arizona Public Service's Four Corners Plant and Colorado/UTE's Hayden Plant. One additional plant which was recommended by the EPA Office of Energy Activities but is not included as a potential plant for this study is Public Service of Colorado's Cherokee Plant. This plant was not included in the potential candidate list since a similar study has previously been completed for Cherokee. However, Public Service of Colorado's Comanche Plant is included in the potential plant site list.

TABLE 3-1. POTENTIAL SOUTHWESTERN POWER PLANTS

Utility	Plant	Location	Capacity, Mw	Type Cooling[1]	Ash Handling[2]	Part. Control[3]	SO_2 Control[4]
Salt River Project	Navajo	Page, Arizona	2,250	WCT	*	*	Planned
Colorado/UTE	Hayden	Hayden, Colorado	163	WCT	WSB	ESP, cyclones	None
Arizona Public Service	Four Corners	Farmington, New Mexico	1,600	CP	WSB WSF	ESP, venturi	UC
Arizona Public Service	Cholla	Joseph City, Arizona	114	CP	WSB WSF	cyclones	Limestone scrubbing
Nevada Power	Gardner	Moapa, Nevada	227	*	*	*	Sodium carbonate scrubbing
Public Service of Colorado	Comanche	Pueblo, Colorado	350	WCT	WSB	ESP, DDF	None
Southern California Edison	Mohave	Laughlin, Nevada	1,580	WCT	WSB DDF	ESP	Planned

*Data not found before Arizona Public Service and Public Service of Colorado indicated an interest in the program.

[1] WCT = wet cooling tower, CP = cooling pond

[2] WSB = wet sluicing of bottom ash, WSF = wet sluicing of fly ash, DDF = dry disposal of fly ash

[3] ESP = electrostatic precipitator

[4] UC = under construction

Sources: NA-205, LE-201, PE-161, EL-094, FE-102, DE-165

Of the seven plants listed in Table 3-1, four use wet cooling towers and two use cooling ponds. No data concerning the type of cooling system used at Nevada Power's Gardner Plant was located before interested plants were identified. Data concerning ash handling was found for five of the seven plants (no data found for Navajo or Gardner). All five of these plants used wet sluicing for bottom ash disposal but only two used wet sluicing for fly ash disposal. Fly ash is disposed of in dry form at Mohave and Comanche. No data concerning fly ash disposal was found for Hayden.

The type of particulate control utilized at the plants in Table 3-1 is in general cyclones and/or electrostatic precipitators with the exception of Four Corners where venturi scrubbers are used on three of the five generating units. No data was located for the Navajo or Gardner Plants concerning particulate control.

The only plants with existing sulfur dioxide control are Cholla and Gardner. Cholla employs limestone wet scrubbing whereas Gardner uses sodium carbonate scrubbing. Some SO_2 removal is observed at Four Corners in the venturi particulate scrubbers (lime is added to the scrubbing system).

3.1.2 Northern Great Plains

The potential power plants for inclusion in the water management study in the Northern Great Plains area are listed in Table 3-2. Three of these plants were included in the recommended plant site list sent to EPA-NERL by the EPA Office of Energy Activities in Denver, Colorado. These three plants are Pacific Power and Light's Johnston Plant, Basin Electric's Leland Olds Plant, and Utah Power and Light's Naughton Plant.

Only one of the plants listed, Minnkota Power Coop's Young Plant, uses cooling ponds for cooling the condenser recirculating water. Two of the plants use once-through cooling exclusively (Leland Olds and Corette) and three others (Bridger, Colstrip and Naughton) utilize wet cooling towers exclusively. Pacific Power and Light's Johnston Plant uses both once-through cooling and wet cooling towers. Cooling towers are used only for one of the four units at the plant (Unit #4). The other three units employ once-through cooling exclusively.

TABLE 3-2. POTENTIAL NORTHERN GREAT PLAINS POWER PLANTS

Utility	Plant	Location	Capacity, Mw	Type Cooling[1]	Ash Handling[2]	Part. Control[3]	SO_2 Control[4]
Basin Electric	Leland Olds	Stanton, N. Dakota	216	OTF	WSB	cyclones	None
Pacific Power & Light	Bridger	Rock Springs, Wyoming	500	WCT	WSB	ESP	None
Pacific Power & Light	Johnston	Glenrock, Wyoming	750	OTF, WCT	WSB, WSF	cyclones, venturi	None
Utah Power & Light	Naughton	Kemmerer, Wyoming	707	WCT	WSB	cyclones, ESP	None
Montana Power Co.	Corette	Billings, Montana	173	OTF	WSB	ESP	None
Montana Power Co.	Colstrip	Colstrip, Montana	700	WCT	WSB (Recirculating), WSF	venturi	Lime/alkaline fly ash scrubbing
Minnkota Power Coop	Young	Center N. Dakota	250	CP	WSB	ESP	UC

---

[1] OTF = once-through fresh water
WCT = wet cooling tower
CP = cooling pond

[2] WSB = wet sluicing of bottom ash, WSF = wet sluicing of fly ash

[3] ESP = electrostatic precipitator

[4] UC = under construction

Sources: NA-205, PE-161, FE-102, EL-094

All of the plants listed in Table 3-2 use wet sluicing to dispose of the bottom ash from the boiler. However, no information concerning fly ash disposal was found for the plants with the exception of Johnston and Colstrip. At Johnston the fly ash from Unit 4 is disposed of in a slurry form (collected in the venturi scrubber). At Colstrip, fly ash from both units is collected by venturi scrubbers and used as a source of alkalinity for removing sulfur dioxide in spray scrubbers. The final disposal product is a mixture of ash and scrubber solids.

Four of the plants utilize electrostatic precipitators for particulate control, one of which combines cyclones and electrostatic precipitators. The Leland Olds Plants uses only cyclones. The Johnston Plant has cyclones on three of the four units and a venturi scrubber on the remaining unit for particulate control.

One of the potential power plants has sulfur dioxide control planned. A lime scrubbing system is under construction at Minnkota Power Coop's Young Plant. Colstrip has existing SO_2 scrubbing on both 350 Mw units (three scrubbing trains per unit).

3.1.3 Southeast

Table 3-3 presents the potential power plants for the water management study for the Southeast. Three of the four plants shown are part of the TVA power generation system (Kingston, Colbert, and Paradise). Kingston and Colbert use fresh water on a once-through basis for cooling. The Paradise Plant uses both once-through cooling and wet cooling towers with the provision of operating Units 1 and 2 with either once-through cooling or with the cooling towers. Unit 3 uses the cooling towers exclusively. Georgia Power's Bowen Plant employs wet cooling towers.

All of the plants shown in Table 3-3 use wet sluicing for disposing of bottom ash and fly ash. All of the plants use electrostatic precipitators for fly ash collection and none of the plants employ sulfur dioxide control.

3.1.4 Northeast

The potential power plants located in the Northeast are shown in Table 3-4. Four of the six plants listed use

TABLE 3-3. POTENTIAL SOUTHEASTERN POWER PLANTS

Utility	Plant	Location	Capacity, Mw	Type Cooling[1]	Ash Handling[2]	Part. Control[3]	SO_2 Control
Tennessee Valley Authority	Kingston	Kingston, Tennessee	1,700	OTF	WSB WSF	ESP	None
Tennessee Valley Authority	Colbert	Pride, Alabama	1,400	OTF	WSB WSF	cyclones, ESP	None
Tennessee Valley Authority	Paradise	Paradise, Kentucky	2,558	WCT, OTF	WSB WSF	ESP	None
Georgia Power Co.	Bowen	Taylorsville, Georgia	1,595[4]	WCT	WSB WSF	ESP	None

[1] OTF = once-through fresh water
WCT = wet cooling tower

[2] WSB = wet sluicing of bottom ash, WSF = wet sluicing of fly ash

[3] ESP = electrostatic precipitator

[4] Plant Capacity as reported in FPC Form 67 Data for 1972; present capacity is 3200 Mw (4 units)

Sources: PE-161, FE-102, EL-094, NA-205

TABLE 3-4. POTENTIAL NORTHEASTERN POWER PLANTS

Utility	Plant	Location	Capacity, Mw	Type Cooling[1]	Ash Handling[2]	Part. Control[3]	SO_2 Control
Niagara-Mohawk	Dunkirk	Dunkirk, New York	628	OTF	WSB	cyclones, ESP	None
Pennsylvania Power & Light	Sunbury	Shamokin Dam, Pennsylvania	410	OTF	WSB	baghouses	None
Pennsylvania Power & Light	Montour	Washingtonville, Pennsylvania	1,500	WCT	WSF WSB	ESP	None
Pennsylvania Electric	Homer City	Homer City, Pennsylvania	1,269	WCT	WSB	ESP	None
Duquesne	Phillips	South Heights, Pennsylvania	410	OTF	WSB	cyclones, ESP	Lime scrubbing
Potomac Electric	Dickerson	Dickerson, Maryland	587	OTF	*	ESP	Magnesium oxide scrubbing

*Data not found before the plant was eliminated from consideration.

[1] OTF = once-through fresh water
$_2$WCT = wet cooling tower

[2] WSB = wet sluicing of bottom ash. WSF = wet sluicing of fly ash

[3] ESP = electrostatic precipitator

Sources: PE-161, FE-102, EL-094, NA-205

once-through cooling. The other two plants, Pennsylvania Electric's Homer City Plant and Pennsylvania Power & Light's Montour Plant, use wet cooling towers. The Dunkirk, Sunbury, Homer City, Montour, and Phillips Plants all use wet sluicing for bottom ash disposal. No data was found concerning bottom ash disposal for Dickerson, or fly ash disposal for any of the plants except Montour, which sluices fly ash on a once-through basis.

Particulate collection is achieved by cyclones and electrostatic precipitators for the Dunkirk and Phillips Plants, electrostatic precipitators for the Homer City, Montour, and Dickerson Plants, and baghouses for the Sunbury Plant. Only two of the six plants have sulfur dioxide control equipment. Duquesne's Phillips Plant uses a lime scrubbing system which started up in 1973 (PE-161). Potomac Electric's Dickerson Plant employs a magnesium oxide scrubbing process which was also started up in 1973 (PE-161).

3.2 Plant Selection

Ten utilities from the geographical regions discussed in the previous section were contacted to determine their interest in the water management program. These utilities are:

1) Salt River Project (Navajo Plant)
2) Arizona Public Service (Four Corners and Cholla Plants)
3) Public Service of Colorado (Comanche Plant)
4) Pacific Power and Light (Johnston Plant)
5) Utah Power and Light (Naughton Plant)
6) Montana Power Co. (Colstrip Plant)
7) Tennessee Valley Authority (Paradise Plant)
8) Georgia Power (Bowen Plant)
9) Duquesne (Phillips Plant)
10) Pennsylvania Power and Light (Montour Plant)

Of these ten utilities, Arizona Public Service, Public Service of Colorado, Georgia Power, Montana Power, and Pennsylvania Power and Light expressed interest in the program. Arizona Public Service wanted to include their Four Corners Plant as opposed to the Cholla Plant since they have been experiencing scaling problems in the venturi particulate scrubbing system at Four Corners.

These five plants (Four Corners, Comanche, Bowen, Montour, and Colstrip) will provide a general spectrum of cooling, ash handling, and pollution control systems for the water management study. Table 3-5 summarizes the data collected for the plants. All of the plants use recirculating cooling systems as opposed to once-through systems. Four of the plants employ wet cooling towers and one (Four Corners) utilizes a cooling pond. These types of cooling systems are more conducive to recycle/reuse alternatives than once-through systems and thus are desirable with respect to the overall objectives of the program.

Four of the plants (Four Corners, Bowen, Montour, and Colstrip) use wet sluicing for fly ash disposal and all of the plants employ wet sluicing for bottom ash disposal. These wet disposal operations will provide greater water recycle/reuse potential for the plants than dry disposal. For example, blowdown water streams that normally are discharged may be used in an ash sluicing system and thus reduce or eliminate the need for fresh water makeup.

All of the plants except Colstrip employ electrostatic precipitation for particulate control. The Four Corners Plant has venturi particulate scrubbers on three of the five generating units and Colstrip has combined particulate and SO_2 scrubbing on both units. The modeling studies associated with the scrubbers will identify water recycle/reuse alternatives at plants using wet scrubbing for particulate and SO_2 control.

Only one of the selected plants has sulfur dioxide control equipment planned. Construction of a lime scrubbing unit is underway at Four Corners. Possibilities for recycle/reuse of normally discarded plant water streams in a sulfur dioxide wet scrubbing system may be studied at Four Corners as well as at Colstrip.

TABLE 3-5. SELECTED PLANTS FOR WATER RECYCLE/REUSE STUDY

Utility	Plant	Location	Capacity, Mw	Type Cooling[1]	Ash Handling[2]	Part. Control[3]	SO_2 Control[4]
Arizona Public Service	Four Corners	Farmington, New Mexico	2,150	CP	WSB WSF	cyclones, ESP, venturi	UC
Public Service of Colorado	Comanche	Pueblo, Colorado	700	WCT	WSB	ESP	None
Georgia Power Co.	Bowen	Taylorsville, Georgia	3,200	WCT	WSB WSF	ESP	None
Pennsylvania Power and Light	Montour	Washingtonville, Pennsylvania	1,500	WCT	WSF WSB	ESP	None
Montana Power Co.	Colstrip	Colstrip, Montana	700	WCT	WSB WSF	venturi	Lime/alkaline fly ash scrubbing

[1] WCT = wet cooling tower, CP = cooling pond

[2] WSB = wet sluicing of bottom ash, WSF = wet sluicing of fly ash

[3] ESP = electrostatic precipitator

[4] UC = under construction

Appendix B. Chemical Characterization of Plant Water Systems

1.0 INTRODUCTION

In order to perform technical and economic evaluations of water recycle/reuse and treatment options for coal-fired power plants, complete characterization of the water of the five generating stations studied was required. Information from the following sources was used:

1) operating and analytical data available from power plants,
2) data from spot sampling and chemical analyses performed, and
3) data on the chemical reactivity of the ash from each plant.

This appendix presents the data acquired from chemical analyses performed on water samples taken at the selected plants. This information corresponds to data source (2) above. The data will be used in conjunction with specific power plant operating and analytical data to:

1) identify quantitatively, existing water management problems of the specific plants,
2) identify potential problem areas,
3) establish the reliability of the simulation model, and
4) be used as inputs for the various recycle/reuse and treatment options studies.

The presentation of the collected data is divided into four sections:

1) sampling,
2) analytical techniques,
3) results, and
4) discussion of results.

2.0 SAMPLING

Five diverse generating stations were sampled to acquire additional information necessary for the characterization of each of their water systems. These plants are:

1) Four Corners Generating Station of Arizona Public Service,
2) Comanche Generating Station of Public Service of Colorado,
3) Bowen Generating Station of Georgia Power Co.,
4) Montour Generating Station of Pennsylvania Power and Light, and
5) Colstrip Generating Station of Montana Power Co.

These five plants provide a general spectrum of cooling, ash handling and pollution control systems for the water management study. Table 2-1 summarizes the major systems at the plants. All of the plants use recirculating cooling systems as opposed to once-through systems. Four of the plants employ wet cooling towers and one (Four Corners) utilizes a cooling pond. Four of the plants (Four Corners, Bowen, Montour, and Colstrip) use wet sluicing for fly ash disposal and all of the plants employ wet sluicing for bottom ash disposal. All of the plants except Colstrip have electrostatic precipitation for particulate control. The Four Corners Plant has venturi particulate scrubbers on three of the five generating units. Colstrip has venturi particulate scrubbers as part of a combined SO_2/particulate removal system on both units.

This section will break down the sampling by plant and will describe:

1) the location of the water streams sampled,
2) the type of samples collected at each point, and
3) the sampling methods employed.

TABLE 2-1. SELECTED PLANTS FOR WATER RECYCLE/REUSE STUDY

Utility	Plant	Location	Capacity, MW	Type Cooling[1]	Ash Handling[2]	Part. Control[3]	SO_2 Control[4]
Arizona Public Service	Four Corners	Farmington, New Mexico	2,150	CP	WSB WSF	ESP, venturi	UC
Public Service of Colorado	Comanche	Pueblo, Colorado	700	WCT	WSB	ESP	None
Georgia Power Co.	Bowen	Taylorsville, Georgia	3,200	WCT	WSB WSF	ESP	None
Pennsylvania Power and Light Co.	Montour	Washingtonville, Pennsylvania	1,500	WCT	WSF WSB	ESP	None
Montana Power Co.	Colstrip	Colstrip, Montana	700	WCT	WSB WSF	venturi	Lime/alkaline fly ash scrubbing

[1] WCT = wet cooling tower, CP = cooling pond

[2] WSB = wet sluicing of bottom ash, WSF = wet sluicing of fly ash

[3] ESP = electrostatic precipitator

[4] UC = under construction

Sources: NA-205, DE-165, PE-161, EL-094, FE-102

2.1 Four Corners Generating Station (Arizona Public Service)

The Arizona Public Service Four Corners Plant is a 2150 Mw coal-fired station located near Farmington, New Mexico. Four Corners uses a cooling pond and bottom ash wet sluicing for all units, particulate wet scrubbing for Units 1-3, and electrostatic precipitators for Units 4 and 5 with dry fly ash disposal.

Makeup water for the plant is taken from the San Juan River and stored in Morgan Lake, which serves as the source for all water used in the system. A periodic blowdown is taken from Morgan Lake to control the dissolved solids concentration and discharged to the Chaco River. Cooling water, bottom ash sluice water, boiler makeup water, and makeup water for the particulate scrubbing system are taken from Morgan Lake.

The particulate scrubbing system consists of six venturi scrubbers (two each for Units 1-3), two thickeners, two thickener transfer tanks for return of thickener overflow and a sluice tank for combining thickener underflows and the scrubber loop bleed stream. The flue gas is contacted with the scrubbing liquor in the venturi throat and upon leaving passes through a disengagement zone where the liquid is separated from the gas and falls into a reservoir at the bottom of the scrubber.

The gas passes through a demister and is then vented to the stack. The liquor collected in the reservoir is recycled for further gas-liquid contact after a bleed stream is removed. The major portion of this bleed stream is routed to a thickener and the remainder is used to reslurry the thickener underflow in the sluice tank before pumping it to the ash pond.

A total of eight aqueous samples were taken to characterize the major water systems at Four Corners and are listed below:

1) plant makeup water from Morgan Lake,
2) effluent liquor from Venturi Scrubbers 1A and 3A,
3) thickener overflow,

4) thickener underflow,

5) bottom ash sluice water,

6) sluice tank effluent,

7) ash pond effluent, and

8) ash pond surface water.

Temperature and pH at each sample point were taken on location. A two-liter grab sample was filtered and acidified with nitric acid for subsequent chemical analysis to determine the concentrations of calcium, magnesium, sodium, potassium, chloride, total sulfur, phosphate, and silicate. Portions of the filtered liquor were taken prior to acidification for use in determining carbonate concentration and, in the case of the scrubber liquor and thickener overflow, the aqueous sulfite concentration. Another grab sample was taken at each point to determine the nitrate concentration, weight percent solids, and total dissolved solids. Representative solid samples of the fly ash and lime were also taken.

2.2 Comanche Generating Station (Public Service of Colorado

The Public Service of Colorado Comanche generating station is a coal-fired system composed of two units, each having 350 Mw capacity, and is located near Pueblo, Colorado. Comanche uses wet cooling towers with the blowdown used for boiler refractory cooling and once-through bottom ash wet sluicing. Hot-side electrostatic precipitators and subsequent dry disposal are employed for fly ash handling.

The water entering the plant is first taken from the Arkansas River and stored in a reservoir. From here a small portion of the raw water is sent to the coal handling facilities for dust suppression. Another portion is sent to the ash removal system to sluice bottom ash. The remainder of the raw water leaving the reservoir is sent to the Comanche lime treatment facility. The calcium carbonate sludge produced is sent to a special pond which is kept separate from the bottom ash ponds. The softened water is used for service water and for makeup water to the two cooling systems.

The water effluent from the overall operation comes from the overflow from the final polishing pond which is fed by the two boiler blowdown streams, the lime sludge disposal pond overflow, and the two bottom ash disposal pond overflows. The final polishing pond effluent is sent to the St. Charles River. The remaining system water losses are cooling tower evaporation and drift and other evaporative losses. Characterization of the Comanche water system was accomplished by sampling the following streams:

1) cooling tower makeup,
2) cooling tower blowdown,
3) bottom ash sluice,
4) ash pond inlet,
5) ash pond subsurface,
6) ash pond effluent, and
7) polishing pond effluent.

The temperature and pH of each sample were recorded on site. A two-liter grab sample was filtered and acidified with nitric acid for subsequent chemical analysis. Portions of the filtered liquors were taken prior to acidification to determine carbonate concentrations. Another grab sample was taken to determine the nitrate, suspended solids, and total dissolved solids concentrations. A representative solid sample of the fly ash was also taken.

2.3 Bowen Generating Station (Georgia Power Co.)

The Georgia Power Co. Bowen Station is a 3180 Mw coal-fired plant located near Taylorsville, Georgia. Bowen employs wet, natural draft cooling towers and once-through bottom and fly ash wet sluicing for all four units.

Makeup water for the plant is taken from the Etowah River and stored in a makeup pond and then used as general service water, boiler makeup, and cooling tower makeup. The general service water effluent is split so that about 5% of the flow returns to the makeup pond and 95% is used as cooling tower makeup. A portion of the cooling tower blowdown is used to sluice bottom ash and fly ash to the ash pond. The excess cooling tower blowdown is discharged as is the ash pond overflow.

The following streams were sampled to characterize the Bowen water system:

1) cooling tower makeup,
2) cooling tower blowdown, Unit #3,
3) bottom ash sluice,
4) fly ash sluice,
5) ash pond subsurface,
6) ash pond effluent, and
7) plant drainoff.

The temperature and pH of each sample were recorded on site. Both filtered and acidified and unfiltered, nonacidified samples were taken for analysis. A representative fly ash sample was also taken.

2.4 Montour SES (Penn. Power & Light)

The Pennsylvania Power and Light Co. Montour Steam-Electric Station is a coal-fired plant with two 750 Mw units located in Washingtonville, Pa. Montour utilizes wet natural draft cooling towers and once-through sluicing of both bottom ash and fly ash with cooling tower blowdown.

Water enters the plant through a raw water reservoir which is fed by the Susquehanna River. Water taken directly from the reservoir is used for cooling tower makeup, boiler makeup, and for general service water. Cooling tower blowdown is used for fly ash, mill rejects, and bottom ash sluicing. The fly ash, mill rejects, and bottom ash are all sluiced to the ash pond which is divided into two large sections.

The ash pond overflow is treated with sulfuric acid for pH control as it enters the detention pond. Other streams flowing into the detention pond include the coal pile runoff, and all miscellaneous plant waste streams. The detention pond overflows into the Chillisquaque Creek. Water losses at the plant occur through cooling tower evaporation and drift, evaporative losses from the ponds, and boiler losses.

A total of ten aqueous samples were taken at the plant and are listed below:

1) ash basin at separating dike,
2) cooling tower makeup,
3) cooling tower blowdown, Unit #1,
4) cooling tower blowdown, Unit #2,
5) detention basin overflow,
6) mill reject slurry,
7) fly ash slurry, Unit #2,
8) ash basin overflow,
9) bottom ash slurry, Unit #1, and
10) miscellaneous wastes.

Temperature and pH of each of the ten samples were taken on location. A two-liter grab sample was taken. One liter of this sample was filtered and acidified with nitric acid for subsequent chemical analysis to determine the concentrations of calcium, magnesium, sodium, potassium, chloride, total sulfur, phosphate, and silica. The cooling tower blowdown and fly ash slurry grab samples were also analyzed for arsenic. A portion of the filtered liquor was taken prior to acidification for use in determining carbonate concentration in each of the ten samples. The remaining liter of sample was used to determine the nitrate concentration, weight percent solids, and total dissolved solids. A solid sample of the fly ash was taken by PP&L personnel. The analytical techniques used for these samples are explained in Section 3.0, and the results are presented in Section 4.0.

2.5 Colstrip SES (Montana Power Co.)

The Montana Power Company Colstrip Steam-Electric Station is a coal-fired plant with two 350 Mw units located in Colstrip, Montana. The Colstrip Plant employs wet forced-draft cooling towers and lime/alkaline fly ash scrubbing for SO_2 and fly ash removal. A recirculating bottom ash sluicing system is also used.

Water from the Yellowstone River is stored in a surge pond from which all plant water is withdrawn. Water taken from the surge pond is processed through a lime softening system. Softened water is used for cooling tower and scrubber makeup water. Cooling tower blowdown is piped to two 12.6 ℓ/sec (200 GPM) capacity brine concentrators. A portion of the distillate provides the demineralizer feed. The remainder of the distillate is used as scrubber makeup. The concentrated waste stream produced is disposed of in two one-acre lined ponds.

There are three identical scrubbing trains on each of the two generating units. The scrubbing system makeup water is added along with lime to the recycle tank in each train. The dust-laden, SO_2-rich flue gas enters the scrubber venturi section at the top of each train and flows down cocurrently with the scrubber recycle liquor. The gas then is channelled through a 180° bend and flows upward through the spray section for SO_2 removal. The scrubbing liquor is sprayed countercurrently to the gas. The spent scrubbing liquor falls into the recycle tank and the clean gas exits at the top of the scrubber, passes through a steam reheat section and an induced draft fan before being vented through the stack.

Mist eliminators are washed by a separate recirculating stream. The wash water is collected by a wash tray and recycled through a wash tray recycle tank. A portion of the wash water is pumped to the wash tray pond for solids settling. Clear liquor is returned to the mist eliminator spray headers. Lime-softened makeup water is added to replace the water lost through evaporation and through occlusion with the solids.

A bleed stream is taken from the scrubber recycle tank, diluted to about 6% solids with slurry pond recycle liquor, and pumped to the pond system. At the present time, scrubber solids are dredged and slurried to a disposal pond.

Bottom ash is sluiced to the bottom ash pond in a recirculating system. Clear liquor from the bottom ash pond clear well is used as sluice water. There are no aqueous discharges from the plant. Water losses occur through cooling tower evaporation and drift, scrubber evaporation, pond evaporation, solids occlusion, and boiler losses.

A total of nine aqueous samples were taken to characterize the Colstrip water system and are listed below:

1) surge pond,
2) cooling tower makeup,
3) cooling tower blowdown,
4) bottom ash sluice water,
5) scrubber recycle slurry,
6) wash tray recycle slurry,
7) fly ash pond recycle,
8) effluent tank, and
9) Pond B overflow to Pond A.

Temperature and pH of each of the nine samples were taken on location. A two-liter grab sample was taken. One liter of this sample was filtered and acidified with nitric acid for subsequent chemical analysis to determine the concentrations of calcium, magnesium, sodium, potassium, chloride, sulfate, phosphate, and silica. A portion of the filtered liquor was taken prior to acidification for use in determining carbonate concentration in each of the nine samples. The remaining liter of sample was used to determine the nitrate concentration, weight percent solids, and total dissolved solids. Sulfite concentrations for the scrubber recycle slurry, wash tray recycle, fly ash pond recycle, and effluent tank samples were determined by difference between the total sulfur concentration of the unfiltered, nonacidified sample and the sulfate concentration of the filtered, acidified sample.

Access to collecting a solid dry fly ash sample was not possible, so a fly ash sample from the J. E. Corette Plant in Billings, Montana was collected by Montana Power Co. personnel. The same coal is burned at both plants. The analytical techniques used for these samples are explained in Section 3.0, and the results are presented in Section 4.0.

3.0 ANALYTICAL TECHNIQUES

The analytical techniques employed to obtain accurate, reproducible analyses of water samples collected from the power plants are described in this section. Analytical techniques were chosen consistent with the accuracy requirements of the simulation model and the levels of concentration of the major ions present in the water samples. Analytical techniques from EPA's "Manual of Methods for Chemical Analysis of Water and Wastes, Standard Methods for the Examination of Water and Wastewater", 13th Ed. (1971), and techniques recommended in EPA Contract CPA 70-143 were utilized in the characterization of the water systems of the generating stations studied in this project.

3.1 Calcium, Magnesium, Sodium, Potassium, and Arsenic

Calcium, magnesium, sodium, potassium, and arsenic ion concentrations were determined by atomic absorption utilizing a Perkin-Elmer, Model 403 spectrophotometer. Dilutions were made with a 1% lanthanum chloride, 5% HCl solution to suppress interference from a number of other ions which occur concurrently in the system. Certified atomic absorptions reference solutions have been used as standards to calibrate the instrument. After dilution of each ion to the proper concentration range, the accuracy of the method is ±2% at the 95% confidence level. The analytical procedures are reported in the EPA's "Manual of Methods for Chemical Analysis of Water and Wastes".

3.2 Chloride

Chloride was determined by specific ion electrode. Samples and standards were run and a calibration curve was prepared. Ionic strength adjusters were added to the samples to give a constant background and eliminate possible interferences.

3.3 Total Sulfur and Sulfate

Total sulfur dissolved in the water samples was measured as sulfate. For total sulfur determinations, all sulfur species are first oxidized to sulfate by hydrogen peroxide. The sulfate was determined by an acid-base titration with standard NaOH after converting all sulfate to sulfuric acid by passage through a hydrogen-form cation-exchange column. This method can be used for sulfate concentrations ranging from 0.001 to 0.5 molar with accuracies of ±2% at the 95% confidence level.

3.4 Carbonate

Liquid phase carbonate concentrations were determined by chemical analyses of the aqueous CO_2 sample utilizing a nondispersive infra-red analyzer. The aqueous CO_2 sample is injected into an acid pool to liberate gaseous CO_2, which is then measured by the nondispersive infra-red analyzer. The accuracy of the technique is ±5% in the carbonate concentration range of the water samples analyzed.

3.5 Nitrate

A specific ion electrode was calibrated and used to determine nitrate ion concentrations after filtering the non-acidified samples. The accuracy of this technique is ±25% at the concentration levels found.

3.6 Phosphate

Phosphate concentrations were determined colorimetrically using the reference method in EPA's "Manual of Methods for Chemical Analysis of Water and Wastes", page 249.

3.7 Silicate

Silica concentrations were determined by the molybdosilicate method in 14th Ed. of "Standard Methods for the Examination of Water and Wastewater". At a pH of about 1.2, ammonium molybdate reacts with silica and phosphate to form heteropoly acids. Oxalic acid is added to destroy the molybdophosphoric acid. The intensity of the yellow color, measured by spectrophotometric methods, is proportional to the concentration of molybdate reactive silica.

3.8 Total Dissolved Solids

Total dissolved solids were determined gravimetrically using the method reported in EPA's "Manual of Methods for Chemical Analysis of Water and Wastes".

3.9 Sulfite

Sulfite ion concentrations were determined by iodometric titration with sodium arsenite. The sample is added to an excess of buffered iodine solution and the iodine remaining after the stoichiometric SO_2 oxidation is titrated with standard sodium arsenite solution employing an amperometric dead-stop method for end-point detection. The accuracy of the technique is ±2% above 0.5 mmole/ℓ.

4.0 RESULTS

The analytical results of the five generating stations studied will be discussed separately. An analysis of the overall accuracy of the analytical measurements will be made by comparing the total ion concentrations measured with the total dissolved solids determined, and by analyzing the computer calculations of ion imbalances based on the pH, temperature, and cation and anion input concentrations. Consistency comparisons of the analytical results with plant design and operating data will be made where possible. Potential problem areas associated with scaling will also be identified.

4.1 Four Corners Generating Station

Results of the chemical analyses of the samples taken at the Four Corners Plant are presented in Table 4-1. The pH, temperature, and dissolved species concentrations are shown for each sample.

The sum of the total ions is shown for comparison to the total dissolved solids to allow a quantitative evaluation of the accuracy of each sample analysis. The % residual electroneutrality is also a measure of the sample consistency.

The analytical results of seven of the nine streams monitored are consistent with the measured total dissolved solids (TDS). The residual electroneutrality for these seven streams as calculated by the equilibrium program reflect ion imbalances of less than 10%. Inconsistencies were identified in the analytical results of the effluent liquor of Venturi Scrubber 3A and the thickener underflow. The solids content (wt. % solids) of the slurry streams were consistent with plant data.

The measured total ion concentration in the Scrubber 3A effluent liquor sample was 9% lower than that indicated by the TDS measurement. The residual electroneutrality indicated an ion imbalance of -22%. This was interpreted as a deficiency of cations when compared to the low total ion concentration indicated by the TDS measurement. A comparison of the chemical analyses of the two scrubber liquors indicated that the measured calcium concentration in Scrubber 3A is low. Duplicate analyses for calcium and sodium confirmed the earlier analyses. Duplicate analyses for total sulfur and total dissolved solids were also

TABLE 4-1. CHEMICAL ANALYSIS OF AQUEOUS SAMPLES OF FOUR CORNERS POWER PLANT ARIZONA PUBLIC SERVICE

Dissolved Solids	Makeup Water	Scrubber Liquor		Thickener Overflow	Thickener Underflow	Bottom Ash Sluice	Sluice Tank Effluent	Ash Pond Effluent	Ash Pond Surface
		1A	3A						
pH	8.1	2.8	3.1	3.8	8.3	6.9	6.7	9.0	8.9
Temperature, °C	17	33	29	33	21	26	26	17	17
Calcium, mg/ℓ	160	790	670	730	330	160	700	650	620
Magnesium, mg/ℓ	40	49	66	54	38	35	46	44	43
Sodium, mg/ℓ	210	290	350	320	280	210	290	280	270
Potassium, mg/ℓ	8	11	14	14	8	8	11	10	10
Chloride, mg/ℓ	110	160	220	180	110	140	160	180	170
Total Sulfur, mg/ℓ as $SO_4^=$	680	2740	2930	2540	1160	690	2110	2040	1880
Sulfite, mg/ℓ as $SO_3^=$	--	8	60	18	--	--	--	--	--
Carbonate, mg/ℓ as $CO_3^=$	77	30	27	16	60	74	21	29	31
Nitrate, mg/ℓ as NO_3^-	9	25	47	24	7	--	20	23	--
Phosphate, mg/ℓ as $PO_4^{\equiv}$	<0.3	2.2	3.5	<0.3	<0.3	<0.3	<0.3	<0,3	<0.3
Silicate, mg/ℓ as $SiO_3^=$	100	270	360	140	150	110	780	730	560
% Suspended Solids	<0.01	2.17	8.80	0.06	10.0	0.04*	2.19	<0.01	0.04
Total Ions, mg/ℓ	1390	4370	4690	4140	2140	1420	4140	3980	3580
Total Dissolved Solids, mg/ℓ	1350	4370	5150	4110	1760	1420	4070	3880	3600
% Residual Electro-neutrality**	+8	-5	-22	-5	+11	+2	+5	-6	+4
Partial Pressure of CO_2, atm	4.8×10^{-4}	1.8×10^{-2}	1.5×10^{-2}	9.6×10^{-3}	2.3×10^{-4}	7.0×10^{-3}	2.6×10^{-3}	1.6×10^{-5}	2.3×10^{-5}
Relative Saturations***									
$CaCO_3$	1.21	7.6×10^{-9}	1.8×10^{-8}	3.8×10^{-7}	3.18	0.11	0.05	7.10	6.37
$CaSO_4 \cdot 2H_2O$	0.21	1.39	1.27	1.28	0.50	0.19	1.19	1.18	1.11

*Not representative

**Does not include silica

***Critical values, above which scale potential exists, are 1.3 - 1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C) made. Initial analytical results were again confirmed. These results indicate that there is a cation other than calcium or sodium in the liquor which has not been accounted for or that there were inconsistencies in the sampling.

Chemical analysis of the thickener underflow sample at Four Corners revealed a 22% greater total ion concentration than the TDS analysis showed. The ion imbalance calculated by the equilibrium program was +11%, indicating an excess of cations. Repeat analyses of the calcium, sodium, total sulfur and TDS confirmed earlier results. These inconsistencies were not resolved. This problem could be related to the high suspended solids in this sample (could have been solid-liquid reactions after the sample was taken) or the pH measurement could have been in error.

Several problem areas with respect to scaling have been identified. Significant calcium carbonate supersaturation was observed in three streams: 1) the thickener underflow (3.2), 2) the ash pond effluent (7.1), and 3) the ash pond surface (6.4). The calcium carbonate precipitation rate studies (see Appendix C) indicated that at relative saturations above 2.5, the precipitation rate increases sharply, indicating a potential for scaling. The calcium carbonate relative saturations for the three streams listed above are all greater than 2.5.

Calcium sulfate dihydrate (gypsum) relative saturations in the critical range (1.2-1.4) were observed in both Scrubber 1A and 3A effluent streams and in the thickener underflow. Gypsum relative saturations greater than 1.1 were also observed in the sluice tank effluent and the ash pond. Drastic differences in the pH of the thickener overflow and underflow were measured. Analytical and computer results indicate that this may be due to poor mixing of the lime with the scrubber effluent liquor in the thickener.

4.2 Comanche Generating Station

Results of the chemical analyses presented in Table 4-2 are, in general, consistent with each other and with plant design and operating data. The sum of all total ions measured were within 6% of the total dissolved solids measured with the exception of the polishing pond effluent (±13%). The electroneutrality balances as calculated by the computer equilibrium program closed within 10% for all streams monitored. None of these samples contained high levels of suspended solids and

TABLE 4-2. CHEMICAL ANALYSIS OF AQUEOUS SAMPLES OF COMANCHE GENERATING STATION PUBLIC SERVICE OF COLORADO

Dissolved Species	Cooling Tower Makeup	Cooling Tower Blowdown	Makeup Ash Sluice	Ash Pond Inlet	Ash Pond Substrate	Ash Pond Effluent	Polishing Pond Effluent
pH	6.20	6.30	8.55	7.45	7.65	7.25	7.70
Temperature, °C	14	22	12	20	24	16	23
Calcium, mg/ℓ	36.5	205	53.4	115	123	105	149
Magnesium, mg/ℓ	10.2	65.5	14.2	18.3	25.5	25.4	33.4
Sodium, mg/ℓ	19	89	19	29	36	44	39
Potassium, mg/ℓ	1.7	13	2.3	3.6	4.7	5.8	6.9
Chloride, mg/ℓ	9	53	7	12	19	16	27
Total Sulfur, mg/ℓ as $SO_4^=$	163	965	134	260	379	355	528
Carbonate, mg/ℓ as $CO_3^=$	6.0	2.7	101	111	86	80	67
Nitrate, mg/ℓ as NO_3^-	9.0	16	13	19	12	17	13
Phosphate, mg/ℓ as $PO_4^=$	0.10	3.5	0.10	0.1	0.6	0.8	2.1
Silicate, mg/ℓ as SiO_3^-	56	280	11	48	94	110	130
% Suspended Solids	<0.01	<0.01	<0.01	0.29	<0.01	<0.01	<0.01
Total Ions, mg/ℓ	311	1690	354	616	779	763	990
Total Dissolved Solids, mg/ℓ	298	1700	345	573	773	763	878
% Residual Electroneutrality*	+9	-10	-5	+8	-2.4	-2	-7
Partial Pressure of CO_2, atm	1.2×10^{-3}	5.6×10^{-4}	2.2×10^{-4}	3.0×10^{-3}	1.6×10^{-3}	3.1×10^{-3}	1.1×10^{-3}
Relative Saturations**							
$CaCO_3$	$1 \times 10^{-}$	$5 \times 10^{-}$	1.56	0.41	0.66	0.12	0.60
$CaSO_4 \cdot 2H_2O$	0.028	0.31	0.031	0.088	0.12	0.11	0.17

*Does not include silica

**Critical values, above which scale potential exists, are 1.3 - 1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C)

significant solid-liquid reaction after the sample was taken is unlikely. This is confirmed by the small electroneutrality imbalances. Concentrations of each ion were consistent with flow rates and evaporation losses reported in plant operating data. The bottom ash sluice water was the only stream which showed any supersaturated species. Computer compilations predicted a calcium carbonate relative saturation of 1.56. Calcium carbonate precipitation rate studies indicate that this is below the critical value for scaling.

4.3 Bowen Generating Station

Chemical analyses of five of the seven streams presented in Table 4-3 were consistent with total dissolved solids, computer equilibrium compilations, and plant operating data. Chemical imbalances were observed in the cooling tower blowdown and the ash pond inlet.

The cooling tower blowdown had a residual electroneutrality imbalance of -13% and an 8% greater total ion concentration than shown by the TDS determination. These values indicate an error in the carbonate concentration measurement. A ±5% error in the carbonate concentration would lower the inconsistencies to within overall analytical error.

The major inconsistency in the analytical results was observed in the TDS of the ash pond inlet stream. The sum of the total ions measured was 35% lower than that indicated by the TDS determination. Repeat analyses of the calcium, magnesium, total sulfur, and TDS confirmed initial results. Silica may account for some of the ion deficiency.

Extremely high calcium carbonate relative saturations were identified in the ash pond inlet, ash pond subsurface, and ash pond effluent samples (38.8, 17.4, 17.1, respectively). These relative saturations are substantially greater than the critical level of about 2.5 as discussed in Appendix C.

4.4 Montour SES (PP&L)

Results of the chemical analyses of the samples taken at the Montour Steam-Electric Station are presented in Table 4-4. The sample showing the largest residual electroneutrality (-18.9%) also shows a discrepancy between total ion and total dissolved solids. The "ash basin at dike" sample analysis yielded a total

TABLE 4-3. CHEMICAL ANALYSIS OF AQUEOUS SAMPLES OF BOWEN GENERATING STATION GEORGIA POWER CO.

Dissolved Species	Cooling Tower Makeup	Cooling Tower Blowdown	Bottom Ash Sluice	Fly Ash Sluice	Ash Pond Subsurface	Ash Pond Effluent	Plant Drainoff Water
pH	7.7	7.9	6.5	11.5	10.4	10.4	8.4
Temperature, °C	21	23	36	29	19	19	21
Calcium, mg/ℓ	6.1	16.1	21.6	311	89	89	18.8
Magnesium, mg/ℓ	1.7	2.1	2.3	<0.10	1.7	1.7	2.0
Sodium, mg/ℓ	1.4	0.2	1.5	9.4	18.7	19.6	1.9
Potassium, mg/ℓ	<0.4	<0.4	1.5	19.8	5.9	5.4	3.5
Chloride, mg/ℓ	2.1	6.4	3.5	3.9	7.7	8.2	18.3
Total Sulfur, mg/ℓ as $SO_4^=$	1.9	3.0	38.4	514	168	182	28.8
Carbonates, mg/ℓ as $CO_3^=$	20.4	43	39	22	24	24	31
Nitrate, mg/ℓ as NO_3^-	4.0	8.4	5.2	9.5	8.9	11.2	10.1
Phosphate, mg/ℓ as $PO_4^=$	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Silicate, mg/ℓ as SiO_3^-	25	28	30	-	53	55	58
% Suspended Solids	<0.01	<0.01	1.11	7.04	<0.01	<0.01	0.09
Total Ions, mg/ℓ	65	107	143	890	377	396	173
Total Dissolved Solids, mg/ℓ	57	93	139	1370	364	374	135
% Residual Electroneutrality*	-4.0	-12.8	-5.0	-3.9	+10.0	+4.0	+6.0
Partial Pressure of CO_2, atm	4.0×10^{-4}	5.3×10^{-4}	9.5×10^{-3}	7.0×10^{-10}	2.0×10^{-7}	2.0×10^{-7}	1.2×10^{-4}
Relative Saturations**							
$CaCO_3$	0.016	0.15	0.01	38.8	17.4	17.1	0.31
$CaSO_4 \cdot 2H_2O$	1.0×10^{-4}	3.0×10^{-3}	5.0×10^{-4}	0.28	0.056	0.058	3.0×10^{-3}

*Does not include silica

**Critical values, above which scale potential exists, are 1.3 - 1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C)

TABLE 4-4. CHEMICAL ANALYSIS OF AQUEOUS SAMPLES OF MONTOUR SES, PENNSYLVANIA POWER AND LIGHT COMPANY

Species	Cooling Tower Makeup	Cooling Tower Blowdown Unit 1	Cooling Tower Blowdown Unit 2	Ash Basin at Dike	Ash Basin Overflow	Detention Basin Overflow	Misc. Wastes	Fly Ash Slurry Unit 2	Bottom Ash Slurry Unit 1	Mill Reject Slurry
pH	8.1	7.8	7.3	8.7	7.7	7.5	7.7	8.9	5.8	6.9
Temperature, °C	5.0	7.0	30.0	11.0	6.5	6.5	10.5	29.5	22.5	17.5
Calcium, mg/ℓ	28.4	43.2	49.7	98.9	98.9	87.4	28.4	142	39.4	39.9
Magnesium, mg/ℓ	5.5	9.5	12.6	10.0	10.0	9.0	6.0	10.4	9.0	11.7
Sodium, mg/ℓ	7.0	10.2	10.2	11.4	11.8	19.1	7.4	12.6	9.8	9.4
Potassium, mg/ℓ	2.6	3.4	2.6	8.2	7.4	6.6	0.9	9.9	5.0	4.2
Chloride, mg/ℓ	19	32	33	33	34	29	18	38	32	33
Total Sulfur, mg/ℓ as $SO_4^{=}$	66	88	131	197	245	215	66	267	101	78
Carbonate, mg/ℓ as $CO_3^{=}$	6.0	9.6	9.0	24	9.6	1.5	10.8	3.8	35.4	7.8
Nitrate, mg/ℓ as NO_3^{-}	5.5	11.8	10.2	6.8	9.9	11.1	5.5	13.3	11.5	11.8
Phosphate, mg/ℓ as $PO_4^{\equiv}$	.029	--	--	--	1.02	.056	--	.224	.046	--
Silica, mg/ℓ as SiO_2	0.9	2.0	3.1	1.4	2.0	1.4	0.6	2.1	2.0	0.5
Arsenic, mg/ℓ as As	--	0.02	0.02	--	--	--	--	0.067	--	--
% Suspended Solids	.0008	.0004	--	.004	.0012	.0016	.0016	2.1	.0532	.0056
Total Ion, mg/ℓ	110	210	261	391	430	380	144	499	245	196
Total Dissolved Solids, mg/ℓ	100	290	250	470	460	290	170	690	200	190
% Residual Electroneutrality*	+4.1	+7.6	+1.8	-18.9	+2.4	+5.3	+3.2	+11.3	+1.2	+12.1
Partial Pressure of CO_2, atm	4.0×10^{-5}	2.8×10^{-4}	2.8×10^{-4}	3.7×10^{-4}	1.5×10^{-4}	3.5×10^{-4}	1.8×10^{-4}	3.2×10^{-5}	1.1×10^{-2}	7.0×10^{-4}
Relative Saturations**										
$CaCO_3$	.013	.037	.025	8.08	.024	.021	.014	6.83	3.8×10^{-2}	.0029
$CaSO_4 \cdot 2H_2O$	.012	.019	.027	.066	.093	.076	.011	.105	.019	.015

*Does not include silica

**Critical values, above which scale potential exists, are 1.3 - 1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C)

ion less than the total dissolved solids measurement which indicates the presence of an unmeasured species. However, this sample is not critical for performing the process simulations of existing operations nor of alternatives.

No samples indicated $CaSO_4 \cdot 2H_2O$ scaling tendencies but the "ash basin at dike" and "Unit #2 fly ash slurry" samples showed $CaCO_3$ relative saturations of 8.08 and 6.83, respectively. However, these samples showed discrepancies in total species and residual electroneutrality which may make the calculated scaling tendencies questionable. No scaling problems have been encountered at Montour although erosive action of the fly ash slurry may keep significant deposits from forming in the fly ash pipeline.

The low $CaSO_4 \cdot 2H_2O$ relative saturations in the cooling tower blowdown samples indicate that the cycles of concentration in the cooling towers can be increased significantly if desired without causing gypsum scale. Acid treatment may be necessary for pH control (to prevent $CaCO_3$ scale) at higher cycles however, depending on the CO_2 equilibrium values in the circulating liquor. This will be determined in the computer simulation studies of existing operations and technical alternatives.

4.5 Colstrip SES (Montana Power Co.)

The results of the chemical analyses of the samples taken at the Colstrip Steam-Electric Station are presented in Table 4-5. As before, the sample location, pH, temperature, and dissolved species concentrations are shown for each of the nine samples. Total ion concentrations compare reasonably well (within 15%) to the TDS determinations except for the surge pond and wash tray recycle samples, which differ by about 20%. The residual electroneutrality for the surge pond sample is +23.8% indicating that an additional anion which was not measured may be present, or that one of the cationic species concentrations is too high. Since the lime softened water results were used as computer inputs, the discrepancy in the surge pond sample was not resolved.

Only one of the nine samples, the bottom ash sluice water, showed a $CaCO_3$ relative saturation greater than the critical value for scaling of about 2.5. The calculated value for this sample is 4.55. The bottom ash sluice water sample also was calculated to have a $CaSO_4 \cdot 2H_2O$ relative saturation of 1.67 which is above the critical level of 1.3-1.4. The erosive nature

TABLE 4-5. CHEMICAL ANALYSIS OF AQUEOUS SAMPLES OF COLSTRIP SES, MONTANA POWER COMPANY

Species	Surge Pond	Cooling Tower Makeup	Cooling Tower Blowdown	Bottom Ash Sluice Water	Scrubber Recycle Slurry	Wash Tray Recycle	Fly Ash Pond Recycle	Effluent Tank	Pond B Overflow to Pond A
pH	6.7	10.3	6.7	10.4	3.9	3.4	5.5	4.4	4.8
Temperature, °C	10.5	6.0	27.5	9.5	50.5	50.5	5.0	17.0	10.5
Calcium, mg/ℓ	57.9	39.9	533	722	504	519	484	497	464
Magnesium, mg/ℓ	19.5	10.7	193	70	5050	2925	1550	2075	1600
Sodium, mg/ℓ	53.5	53.1	710	295	458	153	305	315	345
Potassium, mg/ℓ	4.2	4.2	50.3	13.1	21.9	11.5	13.1	15.5	13.1
Chloride, mg/ℓ	22	17	266	79	129	67	70	74	74
Total Sulfur, mg/ℓ as $SO_4^=$	174	188	3820	2780	19,400	10,600	9000	11,800	9521
Sulfite, mg/ℓ as $SO_3^=$	--	--	--	--	300	1560	400	100	--
Carbonate, mg/ℓ as $CO_3^=$	17.3	6.0	34.8	7.2	52.2	25.2	9.6	31.2	9.0
Nitrate, mg/ℓ as NO_3^-	1.7	1.4	11.2	68	161	80.6	130	118	136
Phosphate, mg/ℓ as $PO_4^≡$	--	--	.26	--	--	--	.009	.028	--
Silica, mg/ℓ as SiO_2	1.8	1.3	5.0	1.4	31	22	24	25	21.4
% Suspended Solids	.002	.0016	.0014	.0048	7.7	.88	.0056	1.36	.01
Total Ion, mg/ℓ	352	322	5624	4036	25,807	14,403	11,586	14,951	12,184
Total Dissolved Solids, mg/ℓ	440	360	6000	4200	29,200	16,300	13,690	17,200	14,400
% Residual Electroneutrality*	+23.8	+7.3	-10.5	-7.9	+11.0	+21.2	-10.6	-13.9	-13.7
Partial Pressure of CO_2, atm	1.9×10^{-3}	1.0×10^{-7}	4.3×10^{-3}	2.6×10^{-8}	5.1×10^{-1}	2.4×10^{-1}	2.4×10^{-3}	1.3×10^{-2}	3.0×10^{-3}
Relative Saturations** $CaCO_3$ $CaSO_4 \cdot 2H_2O$	 .0026 .041	 1.08 .034	 .051 1.11	 4.55 1.67	 1.87×10^{-5} 1.00	 1.2×10^{-6} .82	 2.2×10^{-5} 1.38	 1.5×10^{-6} 1.31	 1.5×10^{-6} 1.30

*Does not include silica

**Critical values, above which scale potential exists, are 1.3 - 1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C)

of the slurry may keep deposits from forming if the water loop is tightened since no scaling problems have been encountered in these areas. The cooling tower blowdown sample shows that the cooling towers cannot be operated at higher cycles of concentration than presently done without producing a gypsum scale potential in the system. To operate the towers at higher cycles would require treatment for calcium removal, such as lime softening of a slipstream of the recirculating water.

APPENDIX C

$CaCO_3$ AND $Mg(OH)_2$ PRECIPITATION KINETICS

1.0 INTRODUCTION

In order to evaluate the technical feasibility of several water recycle/reuse options it is necessary to establish scaling potential criteria for $CaCO_3$ and $Mg(OH)_2$. This appendix describes the studies performed to establish precipitation kinetics data for these two species. Precipitation rates were determined as a function of relative saturation and critical values for scale formation were established at about 2.5 for $CaCO_3$ and 3.4 for $Mg(OH)_2$.

First the results from the literature survey concerning the precipitation kinetics of $CaCO_3$ and $Mg(OH)_2$ are presented. Then the experimental apparatus and procedures are explained followed by discussions of the results.

2.0 LITERATURE SURVEY

The first step in evaluating the precipitation-kinetics of $CaCO_3$ and $Mg(OH)_2$ is to search and retrieve physicochemical and kinetic data from the literature. This section presents a summary of the findings of the literature survey. Information obtained in the areas of solubility, solubility product constants, ion-pair formation, kinetic data, and their respective temperature dependencies will be emphasized.

2.1 Basis of the Literature Survey

The following sources were consulted for this literature survey:

1) Chemical Abstracts - This source was consulted for the period of May 1975 to January 1962.

2) Link, W. F., Solubilities of Inorganic and Metal Organic Compounds - Volume II, Washington, D.C., American Chemical Society.

3) W. L. Badger and Associates, Inc., "Critical Review of Literature on Formation and Prevention of Scale," July 1959, PG-161-399.

4) L. G. Sillen, Stability Constants of Metal-Ion Complexes, London: The Chemical Society, Burlington House, 1964.

2.2 Solubility Data

In this section, temperature-dependent solubility data for the species $CaCO_3$ and $Mg(OH)_2$ will be presented.

2.2.1 $CaCO_3$

Since the equilibrium reactions

$$CO_3{=} + H_2O \rightleftarrows HCO_3{-} + OH{-} \qquad (2\text{-}1)$$

and

$$HCO_3{-} + H_2O \rightleftarrows H_2CO_3 + OH{-} \qquad (2\text{-}2)$$

and $$H_2CO_3 \rightleftarrows H_2O + CO_2 \qquad (2\text{-}3)$$

are appreciable in solution, the solubility of $CaCO_3$ is dependent on the concentration of CO_2 in solution, and therefore on the partial pressure of CO_2 in the atmosphere above the solution. In view of this fact solubility data for $CaCO_3$ can be obtained not only as a function of temperature, but also as a function of partial pressure of CO_2 and pH. Therefore, in Table 2-1, temperature-dependent solubility data taken from Link (LI-001) is presented for $CaCO_3$. In this case the water solution is in contact with ordinary air containing approximately 3.15 parts of CO_2 per 10,000. It is noticed that $CaCO_3$ has an inverse solubility; that is, one that decreases with increasing temperature.

TABLE 2-1. SOLUBILITY OF CALCIUM CARBONATE IN WATER IN CONTACT WITH ORDINARY AIR

T (°C)	Grams $CaCO_3$ per Liter
0	0.081
10	0.070
20	0.065
25	0.056
30	0.052
40	0.044
50	0.038

Also, for comparison we present in Table 2-2 temperature-dependent solubility data for $CaCO_3$ in water essentially free of CO_2. This data is also taken from Link (LI-001). It is clear from this data that the presence of CO_2 has a major effect on the dissolution characteristics of $CaCO_3$.

In view of this fact, it is understandable that solution pH is also important in determining solubility characteristics of this species. Solubility data for $CaCO_3$ at 25°C as a function of pH is presented in Table 2-3. This data is taken from Jaulmes and Brun (JA-105).

TABLE 2-2. SOLUBILITY OF CALCIUM CARBONATE IN WATER ESSENTIALLY FREE OF CARBON DIOXIDE

T (°C)	Grams $CaCO_3$ per Liter
17	0.0145
18	0.0128
25	0.0132
95	0.024
100	0.0375
182	0.025
207	0.014
244	0.011
316	0.080

TABLE 2-3. SOLUBILITY OF CALCIUM CARBONATE AT 25°C AS A FUNCTION OF pH

Grams $CaCO_3$ per Liter	pH
1.87	6
0.35	7
0.10	8
0.032	9
0.012	10
0.0077	11
0.0071	12
0.0071	13
0.0070	14

2.2.2 $Mg(OH)_2$

According to Gjalbaeck (GJ-001), $Mg(OH)_2$ exists in two well defined modifications of which the more soluble is the labile phase and the less soluble is the stable phase. At a temperature of 18°C, the following comparative results are reported (LI-001).

Method	Solubility (moles/liter) Stable Phase	Solubility (moles/liter) Labile Phase
Direct Determination	2.2×10^{-4}	6.5×10^{-4}
$Mg^{+2} + 2NH_4OH \rightleftarrows Mg(OH)_2 + NH_4^+$	1.9×10^{-4}	5.5×10^{-4}
Conductivity Method	1.35×10^{-4}	4.6×10^{-4}
Electrometric Method	1.6×10^{-4}	7.0×10^{-4}

Temperature-dependent solubility data for $Mg(OH)_2$, taken from Link (LI-001), is presented in Table 2-4.

TABLE 2-4. SOLUBILITY OF MAGNESIUM HYDROXIDE IN WATER

T (°C)	Moles $Mg(OH)_2$ per Liter
18	0.000200
25	0.000197
35	0.000169
45	0.000150
75	0.000118
100	0.000072
110	0.000074
142	0.000042
150	0.000037
158	0.000031

2.3 Solubility Product Data

For this program, precipitation rate data will be expressed as a function of the relative saturation of the particular precipitating species in solution. The relative saturation is defined as the ratio of the solution activity product for the precipitating species (in the case of $CaCO_3$, $a_{Ca^{+2}} \times a_{CO_3^{-2}}$) to the equilibrium solubility product, Ksp, for the precipitating species at the temperature T. Therefore, information on the temperature dependence of the solubility products for $CaCO_3$ and $Mg(OH)_2$ is necessary for these studies.

Data has been previously compiled concerning the temperature dependence of solubility for these species for use in the equilibrium program. However, in this section solubility product data that is available from other independent sources will be presented.

2.3.1 $CaCO_3$

Giringhelli and Bianucci (GH-001) have determined the solubility product constant for $CaCO_3$ in the temperature range 0 to 50°C in water saturated with CO_2 at an equilibrium partial pressure of 0.0004 atmospheres. Their data is presented in Table 2-5.

TABLE 2-5. SOLUBILITY PRODUCT CONSTANT FOR $CaCO_3$ IN H_2O SATURATED WITH CO_2

T (°C)	Ksp
0	6.0×10^{-9}
10	4.5×10^{-9}
20	3.4×10^{-9}
25	2.9×10^{-9}
30	2.5×10^{-9}
40	1.9×10^{-9}
50	1.4×10^{-9}

2.3.2 $Mg(OH)_2$

Feitknecht and Schindler (FE-105) have reported values for the solubility product constant of $Mg(OH)_2$ at 25°C. For the labile phase of $Mg(OH)_2$, they report a Ksp of 6.32×10^{-6}; and for the stable phase, a Ksp of 1.26×10^{-11}.

No literature information was found that gave the temperature dependence of the solubility product for $Mg(OH)_2$. However, temperature-dependent solubility product data for this species has been previously determined for use in the equilibrium computer program. From available thermodynamic data the temperature dependence of the solubility product constant was calculated by using the integrated Gibbs-Helmholtz equation.

2.4 Dissociation and Ion Pairing Data

No information was found in the literature that gave the temperature dependence of the dissociation constants for the ion-pairs $CaCO_3°$ and $Mg(OH)^+$. However, temperature-dependent dissociation constants for $CaCO_3°$ and $Mg(OH)^+$ have been previously determined by calculations using the Fuoss equation (FU-001) for use in the equilibrium program.

2.5 Formation Kinetic Data

In this section data available on the formation kinetics of solid $CaCO_3$ and $Mg(OH)_2$ will be presented.

2.5.1 $CaCO_3$

In 1965, R. Pytkowicz (PY-010) published an experimental study of the rate of $CaCO_3$ nucleation over a wide range of carbonate concentrations in natural and artificial sea waters. This work was performed in order to study factors affecting the induction period of nucleation at high supersaturations, and to permit extrapolation of nucleation rate data to low supersaturations.

In his experimental study, sodium carbonate solutions were added to natural and artificial sea water, prepared by the method of Lyman and Fleming (LY-001), with the original ionic strength maintained by adding sodium chloride. In some cases, sodium bicarbonate was also added to determine the effect of changes in pH on the induction period. The time of nucleation and solution pH were determined.

In Figure 2-1, the results of the addition of 8.25 mmoles/liter of Na_2CO_3 to four natural sea water samples are shown. The variation of solution pH is shown versus time.

Various amounts of Na_2CO_3 were added to samples of filtered and unfiltered natural sea water, and the time of nucleation or induction period was determined. Na_2CO_3 and 2 mmoles/liter of $NaHCO_3$ were added to some of the samples and these results are shown in Figure 2-2.

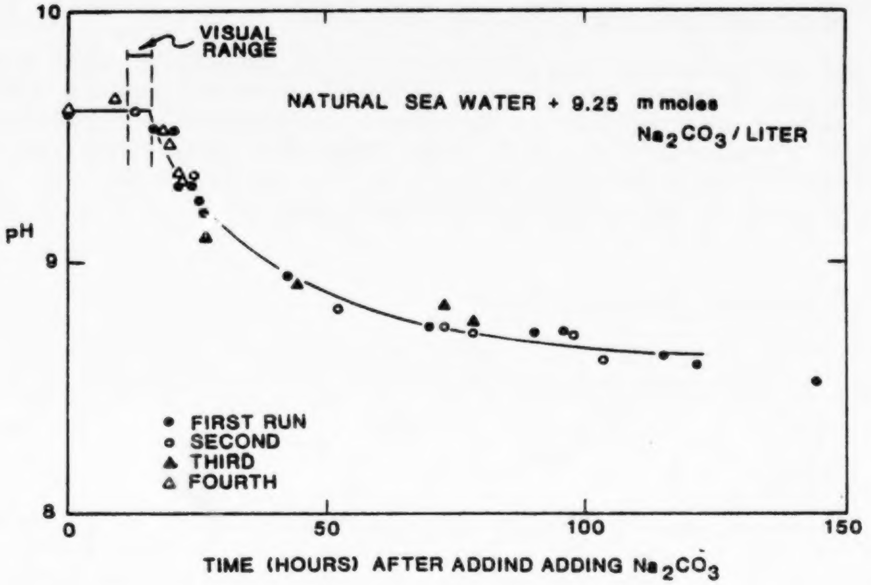

Figure 2-1. Visual and pH determination of the time of nucleation.

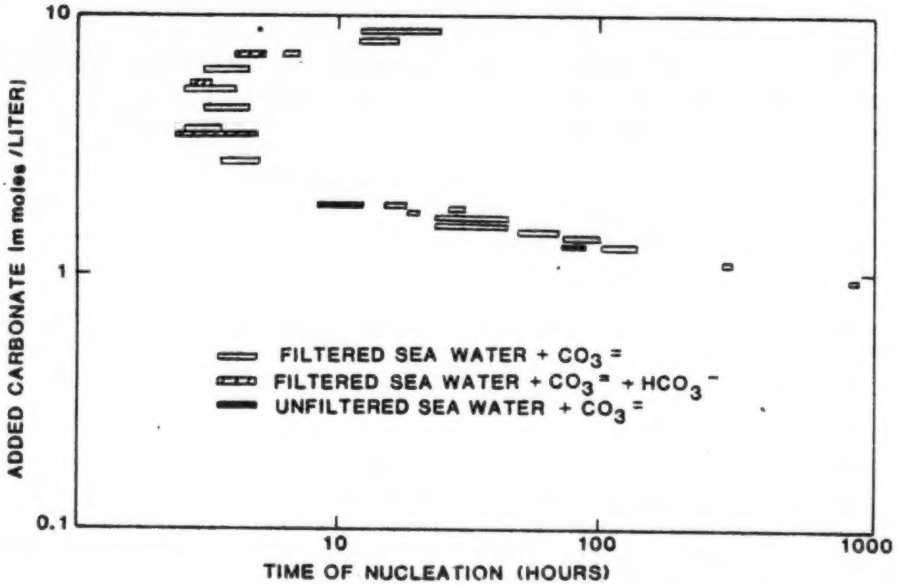

Figure 2-2. Time of nucleation versus initial carbonate concentration.

The effect of magnesium on the time of nucleation was studied by adding Na_2CO_3 to magnesium-free artificial sea water, and to natural sea water that was enriched with magnesium. The results are compared in Table 2-6 with selected values from Figure 2-2.

Pytkowicz observed that at very high carbonate concentrations the nucleation was slowed by further addition of carbonate, as is shown in Figure 2-2. He also observed that magnesium-free artificial sea water yielded much shorter times of nucleation than did natural sea water, and that it did not produce the minimum time of nucleation observed in Figure 2-2. From Table 2-6 it can be seen that enrichment with magnesium decreased the rate of nucleation. Log-log plots of the time of nucleation versus the carbonate concentration showed a second-order decay of the nucleation time with increasing carbonate concentration in magnesium-free artificial sea water. A sixth-order decay was found in natural sea water.

TABLE 2-6. TIME OF NUCLEATION RESULTING FROM ADDED CARBONATE

	Added Carbonate (mmole/1)	Time of Nucleation
A. Magnesium-free artificial sea water	7.34 4.58 1.83 0.93	1.0 min. 4.7 min. 13 min. 20 min.
B. Natural sea water (selected values to match (A))	7.35 4.58 1.83 0.93	6.0-7.0 hr. 3.0-4.5 hr. 15-18 hr. 900-940 hr.
C. Natural sea water enriched in magnesium to about twice the original concentration	4.75 3.85	22-53 hr. 22-53 hr.

Pytkowicz stated that his results suggest that many more collisions of carbonate ions are necessary to form $CaCO_3$ nuclei in the presence of magnesium. Also, it is apparent that magnesium inhibits the formation of $CaCO_3$ nuclei and is the predominant factor in determining the time of nucleation at high carbonate concentrations.

2.5.2 $Mg(OH)_2$

In 1967, David Klein et al., (KL-052) performed an experimental study of the homogeneous nucleation of $Mg(OH)_2$. They asserted that the rate of homogeneous nucleation of $Mg(OH)_2$ precipitating from solution could be written as

$$dN/dt = k\ (IP)^n \qquad (2\text{-}4)$$

where

N = number of nuclei formed

t = time

(IP) = ion activity product or a_{Mg} + 2 x $a_{OH^-}{}^{2}$

n = number of $Mg(OH)_2$ units in the nucleus (KL-053, KL-054)

It is known from the theory of homogeneous nucleation from dilute solutions by Nielsen (NI-001) that the chief parameters which determine nucleation rate are the salt-solution interfacial tension, the supersaturation of the solution, and the number of ions in the nucleus. Therefore, determining the rate of nucleation as a function of the ion product provides a conceptually simple means for determining the size of the precipitation nucleus.

In their experimental study magnesium ion and hydroxide ion were generated simultaneously in stoichiometric amounts by electrolysis of a 0.1M solution of $NaNO_3$ with a magnesium anode and a platinum cathode. Precautions were taken to remove most, if not all, of the foreign particles from the solution to insure homogeneous nucleation. This was accomplished by continuously pumping the solution from the cell through a fiberglas filter mat and back into the cell. At intervals during the electrolysis a sample was removed and the number of particles present in it was counted by using a Coulter electronic particle counter with a 30 micron orifice. Also, the necessary analytical determinations were made on each sample.

The results of one of their typical experiments is shown in Figure 2-3. The solution pH and total number of particles are plotted versus time duration of the experiment. The maximum rate of formation of particles occurs at approximately the maximum pH of the solution.

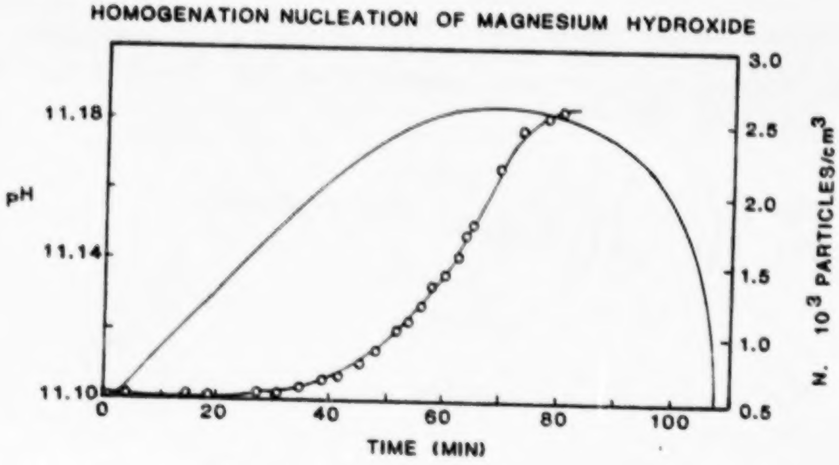

Figure 2-3. Variation with time, of pH (upper curve) and of number of particules, during an experiment.

The results of four of their experiments are presented in Figure 2-4. In this figure, the log of dN/dt is plotted versus the log of the ion activity product. The least-squares slope for the points of Figure 2-4 is 33±4 and so the best value for the number of $Mg(OH)_2$ units in the nucleus is 33.

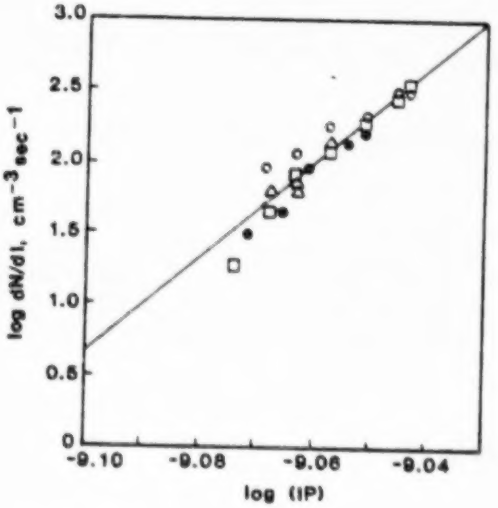

Figure 2-4. Dependence of rate of nucleation (particles/cm³ sec) on solution concentration expressed as (IP) $(a_{Mg}a_{OH})$.

These researchers also made a comparison of their experimental nucleation rate data with theoretical estimates. They used the following theoretical expression for the rate of homogeneous nucleation (NI-001):

$$dN/dt = \left(\frac{D}{d^2 \nu_o}\right)\left(\frac{2}{3\pi kTn^*}\right)^{\frac{1}{2}} \exp\left(-\Delta G^*/kT\right) \qquad (2\text{-}5)$$

where

dN/dt = rate of nucleation

D = diffusion coefficient of $Mg(OH)_2$

d = mean diameter of one Mg^+ and two OH^- ions

ν_o = molecular volume of solvent

$\phi = kT \ln S = kT \ln \left((IP)/Ksp\right)^{1/3}$

n^* = number of ions in the nucleus

ΔG^* = free energy of nucleation

By using their experimental values for dN/dt at particular ion activity products (IP) they were able to calculate a free energy of nucleation (ΔG^*) from Equation 2-5 for the $Mg(OH)_2$ precipitation process. This value based on experimental data was compared with a theoretical thermodynamic value calculated from Gibb's equation:

$$G^* = \phi n^*/2$$

The two values agreed closely indicating that homogeneous nucleation of $Mg(OH)_2$ was indeed observed and that the critical nuclei size was approximately 33 $Mg(OH)_2$ units.

3.0 APPARATUS AND PROCEDURES

This section presents detailed descriptions of the experimental apparatus and procedures used to correlate precipitation rates with relative saturation for $CaCO_3$ and $Mg(OH)_2$. First the batch solid reactor is described along with the ancilliary equipment followed by a discussion of the experimental and analytical procedures involved.

3.1 Description of Experimental Apparatus

The major experimental apparatus used in this precipitation kinetics study is illustrated in Figure 3-1. The experiments are centered around the batch-solid crystallizer shown in Figure 3-2.

3.1.1 Inlet Feed Systems

Supersaturated reactor solutions are produced by introducing two separate feed solutions at constant flow rates into the well stirred reactor. In the case of the $CaCO_3$ study, $CaCl_2$ and Na_2CO_3 of predetermined concentration are used as the stock feed solutions. These solutions are made up quantitatively prior to a run and stored respectively in two covered 16 gallon Nalgene feed containers. Eastern Industries circulating pumps are used to remove the feed liquor from the storage containers through outlet ports at the bottom. From the pumps, a line is returned to the storage containers in order to release excessive head pressures from the pumps and to continuously circulate feed solution (see Figure 3-1). Another line from the pump outlet is directed to the Moore (Model 63-SD) constant differential pressure regulators used to maintain a constant hydraulic pressure drop across the Whitey control valves. This control system thus maintains a constant predetermined feed liquor flow rate regardless of possible head pressure fluctuations.

The regulator system is followed by Matheson (Model 7641) flowmeter units, calibrated to 1% accuracy, and used to measure the constant feed solution flow rates. A constant and accurate flow rate is important since the steady state precipitation rate calculations employ this experimental parameter.

From the flowmeter units the feed streams are directed to stainless steel tubing coils immersed in the constant temperature water bath before entering the reactor. By heat transfer, the feed solutions are thus preheated to the desired reaction temperature prior to entering the reactor.

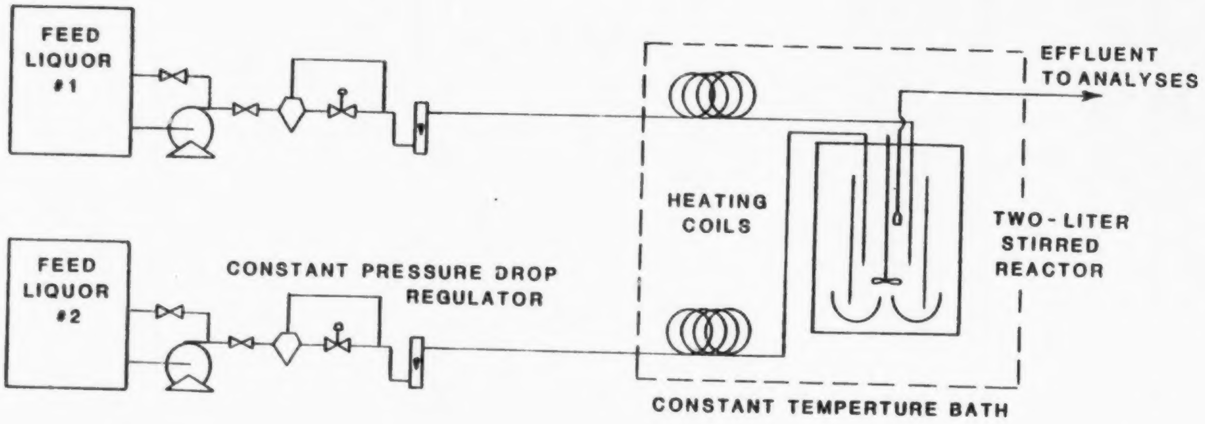

Figure 3-1. Experimental system for liquid-phase reaction study.

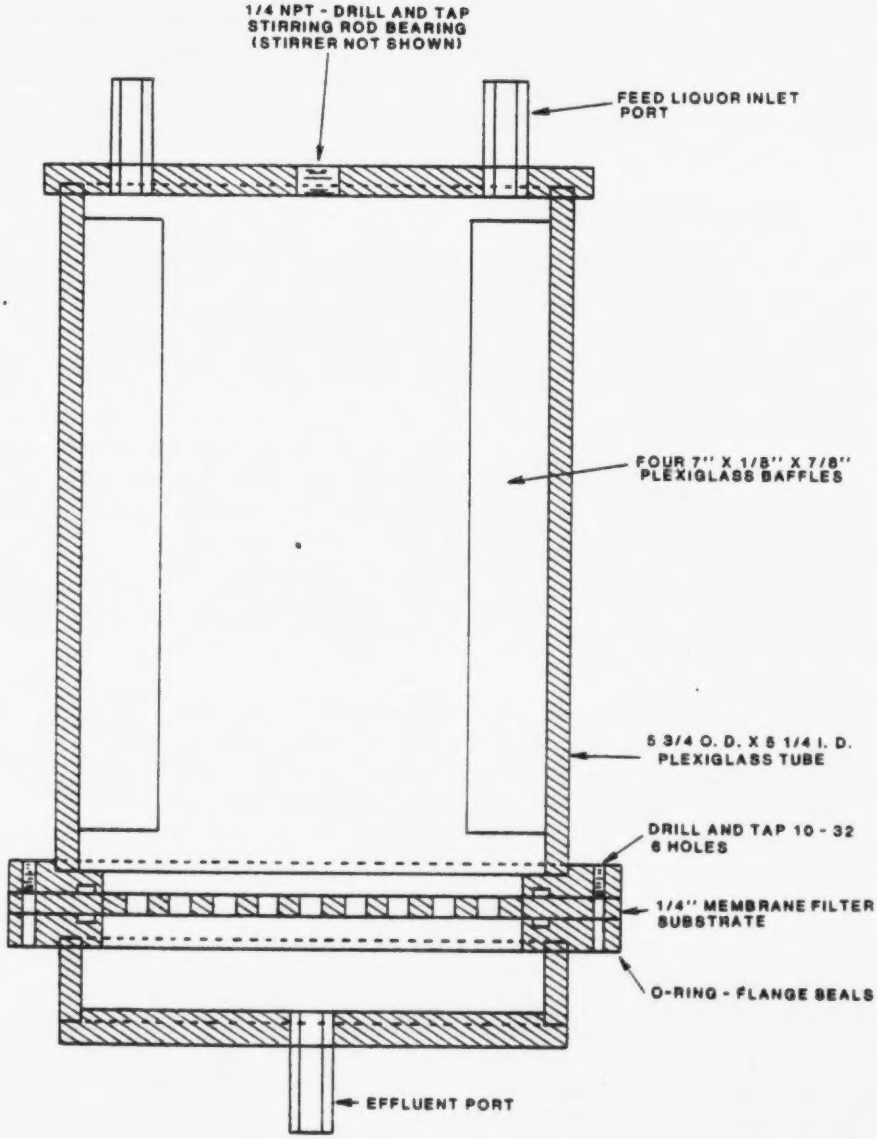

Figure 3-2. Batch-solid reactor.

Within the reactor, precipitation from the supersaturated solution is initiated by seed crystals which are retained within the reactor cavity by a filter membrane. The effluent stream from the reactor is directed to a five-neck round bottom flask supported in the constant temperature bath. This flask contains pH and reference electrodes thus allowing continuous monitoring of the effluent stream pH while maintaining reaction temperature. From this point, the reactor effluent stream can be sampled and the various analytical determinations performed.

3.1.2 Batch-Solid Reactor

The unique batch-solid crystallizer, designed and constructed for these kinetics experiments, is shown in Figure 3-2. The reactor is based upon conventional O-ring-flange design techniques for ease of assembly and breakdown for cleaning. The reactor is constructed primarily from inert Plexiglass material.

A 1/10 horsepower, A.C. variable-speed electric motor (not shown in Figure 3-2) is mounted on the top plate of the reactor and is connected to a Nalgene stirring rod via a 1/4" universal joint. The stirring rod, in combination with the baffled tube-reactor cavity, provide a continuously mixed suspension of seed crystals in the supersaturated liquor. The stirring speed can be controlled up to a maximum speed of 500 RPM.

Also mounted in the top plate of the reactor are the two plexiglass inlet feed ports and the nylon Swagelok thermometer port. The vacuum and pressure tight stirring rod bearing, made from a 1/4" nylon Cajon male connector, is mounted on the top plate along the longitudinal axis.

The solids are retained within the reactor cavity by a Millipore filter membrane supported by a 1/4" thick perforated Plexiglass substrate. The membrane-substrate combination is sandwiched between the upper and lower portions of the reactor by O-ring-flange seals. The effluent stream thus exits from the bottom portion of the reactor while seed and product crystals remain in the upper portion. The volume of the reactor cavity is approximately three liters.

3.2 Experimental Procedures

This section includes a descriptive presentation of the preparation and experimental procedures developed specifically for the $CaCO_3$ and $Mg(OH)_2$ kinetics studies.

3.2.1 Preparation of Feed Solutions

The $CaCO_3$ precipitation kinetics study uses two separate feed solutions, $CaCl_2$ and Na_2CO_3. For the $Mg(OH)_2$ study, the feed solutions are NaOH and $MgCl_2$. The above feed solutions are prepared and standardized for their respective concentrations before starting each experimental run. The solids of each feed compound are dissolved in a small volume (0.5 to 1.0 liter) of deionized water. They are quantitatively transferred to the two large polyethylene feed tanks, diluted with deionized water to approximately 30 liters, and stirred to obtain a homogenous solution. Contamination and oxidation are minimized by using polyethylene floating lids and tank covers.

Analyses of calcium, magnesium and sodium are used to determine the concentrations of their respective feed solutions. A 200 ml sample from each feed solution is sufficient for all analyses. Each sample is stored in a polyethylene bottle and labeled with the necessary information such as: run number, date, time, solution identification and operator's initials.

3.2.2 Preparation of Batch-Solid Crystallizer

The reactor vessel is washed and rinsed thoroughly before assembly. A mild detergent and soft brush is used to prevent excessive scratching of the Plexiglass reactor. Deionized water is used to remove all traces of detergent and foreign material.

The bottom portion of the reactor vessel is then filled with deionized water to prevent the formation of air pockets below the filter membrane. This will also insure a constant outlet flow from the reactor. With the membrane support plate positioned correctly on top of the bottom portion of the reactor, a tared 142 mm Millipore filter membrane is then carefully placed on the support plate. The top portion is placed in position and reactor assembly is completed. A filter membrane with 0.8μ pore size is used for the $CaCO_3$ precipitation kinetics study; 0.45μ to 0.6μ pore size is used for the $Mg(OH)_2$ study.

Before placing the assembled reactor in the constant temperature bath, the outlet stream line is connected. The reactor is then filled to approximately one-half capacity with deionized water and the remainder with feed solutions before adding a predetermined amount of seed crystals with stirring.

Inlet stream flowmeters are roughly adjusted by flushing the system with approximately 1.0 liter of the feed solutions. After flushing both inlet streams, samples for inlet feed concentrations are taken. Inlet feed lines are attached and the reactor is filled to capacity with equal volumes of feed solutions, seed crystals are then added, and the system is then placed in the bath. The stirrer blade is positioned approximately 3 cm above the filter membrane and is maintained at a proper stirring speed by the variable control mounted on the control panel.

While the reactor temperature is stabilizing, the 0.5 liter round-bottom five-neck flask is assembled and placed in the constant temperature bath. This flask allows continuous accurate monitoring of reactor effluent temperature and pH.

3.2.3 Experimental Run Procedure

When all preparations have been completed and the charged reactor has reached constant temperature, the experiment can proceed. The timing device and inlet feed stream pumps are started with the inlet return valves opened completely. Inlet stream flowmeters are adjusted as accurately as possible. Both inlet streams and the reactor outlet stream are controlled by identical flowmeters. The calibration graphs provided with the Matheson Model 7641 flowmeters are referred to for the proper settings. The Moore Model 63-SD constant differential pressure flow controllers located in both inlet feed streams automatically maintain the desired constant flow rate for the duration of the experiment. However, continuous observation and manual fine adjustments may also be necessary.

Initial samples are taken immediately after the system has been properly adjusted. Refer to the sampling scheme for the correct procedure. A three-way teflon valve located on the control panel simplifies the actual sampling of the reactor outlet stream. The determinations of (Ca^{++}), (Mg^{++}), pH and temperature are performed during the actual experiment. The remaining determinations of (Na^{+}), (Cl^{-}), alkalinity, and ($CO_3^{=}$) are performed upon completion of the experiment. The data including technical observations are recorded in an experimental log book. Samples are taken at predetermined intervals and monitored until a steady-state precipitation rate is attained.

Upon completion of an experimental run, the inlet feed lines and stirring-motor assembly are disconnected from the reactor. The remaining liquor above the filter membrane is siphoned off by leaving the outlet reactor stream open. Deionized water is used to wash down the stirrer blade, sides and rim of the reactor in order to collect an accurate total of product crystals. When the liquid level drops below the filter membrane, the reactor is removed from the constant-temperature bath and dissembled. The filter membrane plus product are dried at 50-60°C, for 48 hours. Determination of the weight of product crystals is performed by subtracting the weight of the filter membrane and seed crystals from the total weight. Photomicrographs of the seed crystals and product crystals at comparative magnifications are performed in order to determine crystal size and growth characteristics.

3.2.4 Sampling Scheme for Experimental Run Procedure

The sample scheme for both precipitation kinetics studies are identical with one exception. During the $CaCO_3$ study, a separate sample for the ($CO_3^=$) analysis is taken.

Polyethylene bottles for the collection of samples are prepared in advance of an experimental run. Each bottle is cleaned, dried, labeled and tarred before the addition of deionized water which serves as the dilutant. It is then weighed again to determine the exact amount of deionized water added in order to accurately determine the dilution factor for that particular sample. Inlet feed samples are not diluted, but a sufficient dilution factor must be approximated before intermediate and steady-state samples are taken in order to maintain a relative supersaturation <1.0 in the sample bottle.

3.2.4.1 Inlet Feed Solutions

Two clean 0.5 liter polyethylene bottles are filled with the two feed solutions from the reactor inlet feed lines after the system is adequately flushed. This amount of sample insures that additional determinations can be made if necessary. Each bottle is labeled with the run number, solution identification, approximate concentration, date and operator's initials. Determination of (Ca^{++}) or (Mg^{++}) and (Na^+) is performed on these samples after completion of the experiment.

A tarred 60 ml polyethylene bottle containing a known amount of NH_4-EDTA buffer solution is filled with the Na_2CO_3 feed solution from the reactor inlet feed line. The bottle is capped tightly and shaken. Before capping the bottle, it is reweighed to determine the dilution factor. Each bottle is labeled with the run number, sample identification, dilution factor, weights, date and operator's initials.

3.2.4.2 Intermediate Diluted Filtrate Samples

At predetermined intervals during an actual experimental run, samples of the effluent are taken in order to determine when steady-state is attained. A tarred 0.5 liter polyethylene bottle containing a known amount of deionized water for quenching purposes is filled to a specific total volume with sample. The bottle is capped tightly and shaken immediately. The dilution factor is calculated and recorded on the bottle with the run number, sample identification, elapsed time in minutes, date, weights and operator's initials. The determination of (Ca^{++}) or (Mg^{++}) is performed on these samples using a direct colorimetric titration method summarized in Section 3.3.

3.2.4.3 Steady-State Diluted Filtrate Samples

Upon reaching steady-state, diluted filtrate samples are taken in the same manner as described in Section 3.2.4.2. A minimum volume of 500 mls of diluted filtrate is sufficient to perform the analyses of all major species in duplicate with an adequate amount of sample left in reserve for additional determinations if necessary. The methods of analyses for all of the major species in both precipitation kinetics studies are summarized in Section 3.3.

3.3 Analytical Procedures

This section describes the analytical procedures for the determination of the principal ionic species encountered in the precipitation kinetics studies on $CaCO_3$ and $Mg(OH)_2$.

3.3.1 Determination of Sodium, Calcium and Magnesium

Samples taken from the inlet and outlet streams are diluted with a lanthanum stock solution to control known interferences. With an accurately determined dilution step, the samples are aspirated directly into the atomic absorption spectrophotometer for measurement of their respective concentrations.

Intermediate samples taken during the experimental runs are analyzed for calcium or magnesium to determine when the steady-state condition is reached. This procedure utilizes a colorimetric titration with diNa-EDTA and Calgamite indicator. Analyses of these intermediate samples are repeated with atomic absorption to verify the steady-state condition.

3.3.2 Determination of Chloride

Chloride present in the inlet and outlet streams is determined by a manual potentiometric titration. The procedure uses the millivolt scale of a pH meter to determine the end point of the titration with 0.02M $AgNO_3$. A cup-type silver electrode (Fisher No. 13-639-122) in conjunction with a silver-silver chloride reference electrode with a sodium sulfate bridge (Fisher No. 9-313-216) are used in this procedure.

3.3.3 Determination for Alkalinity

Hydroxyl ions present in the liquid samples by virtue of the dissociation of solutes are neutralized by an electrometric titration with a standard acid. A Beckman Century SS-1 pH meter equipped with a calomel reference electrode and a standard glass pH electrode are used in this procedure.

3.3.4 Determination of Total Carbonate

Carbon dioxide evolved from the reaction of a liquid sample injected into a buffered acid pool is measured by a non-dispersive infrared analyzer. The instrument allows samples to be analyzed without introducing atmospheric carbon dioxide into the system and removes harmful water vapor prior to reaching the infrared cell. The amount of CO_2 in the injection ampule is monitored by a recorder equipped with a disc-chart integrator to measure the peak area. This peak area is used instead of the peak height to accurately determine the amount of CO_2 present in the sample because of pH fluctuations in the acid pool.

4.0 EXPERIMENTAL RESULTS FOR $CaCO_3$

This section presents the results of the experiments performed to determine $CaCO_3$ precipitation kinetics. First the method used for correlating the data is described. Then the actual data is presented in both tabular and graphical form and discussed.

4.1 Kinetics Data Processing

For the batch-solid kinetics experiments, a steady-state precipitation rate can be calculated from a straightforward material balance. Steady-state material balances may be written for the reactor in terms of either total calcium or total carbonate. That is:

$$(F_i \cdot C_i)_{inlet} - (F_i \cdot C_i)_{outlet} = R = \text{Precipitation Rate} \qquad (4\text{-}1)$$

where F_i = flow rate in (ℓ/min),

C_i = concentration in (mMoles/ℓ),

R = rate of precipitation in (mMoles/min), and

i = calcium or carbonate.

Thus, equation 4-1 expresses the difference in the rate of material entering and leaving the reactor, and this difference is the rate at which solid material is produced in the reactor, or the rate of precipitation. This precipitation rate is calculated then by measuring the feed and effluent flow rates and determining the concentrations by analytical means for each kinetics experiment.

An additional check is provided by a total solids material balance. That is, the amount of product solids for a run is determined by emptying the reactor through the bottom port following shutdown so that the solids are retained on the filter membrane. After drying, the product cake is weighed and compared to the amount of seed material introduced initially. This mass difference is equal to the time integral of the experimental reaction rate multiplied by the $CaCO_3$ molecular weight. This corresponds closely to the experimental steady-state precipitation rate multiplied by the total run time, since the reactor composition approaches steady-state in a short period of time compared to the total time duration of the run.

The $CaCO_3$ precipitation rate, R, determined for a particular run in the above manner, is expressed as a function of the steady-state relative saturation. The relative saturation is defined as the ratio of the reactor solution activity product for the precipitating species, in this case, $a_{CO_3^{+2}} \cdot a_{CO_3^{-2}}$, to the equilibrium solubility product, Ksp, for $CaCO_3$. Activities for the particular solution species are calculated by inputting pertinent reactor solution information, such as concentrations of calcium, chloride, sodium, and carbonate, pH, and temperature, to the chemical equilibrium computer program. Reactor solution relative saturations are controlled experimentally by varying the mean reactor residence time or the inlet feed compositions from run to run.

A suitable rate expression for $CaCO_3$ solid precipitation from supersaturated liquor may be written in the following form:

$$R = k \cdot M \cdot \phi \qquad (4\text{-}2)$$

where: R = rate of solid precipitation,

k = rate constant, which may vary with liquor temperature, composition, and transport parameters,

ϕ = driving force term related to the degree of $CaCO_3$ supersaturation,

M = term dependent on the amount of solid phase present.

The term, M, is usually assumed to be proportional to the exposed surface area of the solid phase. This is obviously difficult to quantify in experiments with suspensions of many fine particles of seed crystals; therefore, no crystal surface area measurements were attempted. Normally, as in this case of $CaCO_3$ precipitation kinetics, the term is equated to the mass of initial seed crystals and therefore has the units of "grams."

For dissolution and precipitation reactions, ϕ, the driving force term, is usually taken to be the difference between the actual and equilibrium quantities of the reacting species, perhaps raised to some power. If one assumes a linear dependence of precipitation rate on the driving force function, then equation 4-2 can be written as:

$$R(\text{mMoles/min}) = k(\text{mMoles/gram-min}) \cdot M(\text{grams}) \cdot (\text{R.S.}-1) \quad (4\text{-}3)$$

where R.S. is the solution relative saturation as defined earlier. In this study, the precipitation rate divided by the mass of seed crystals (10.0 grams) is analyzed in terms of the solution relative saturation.

4.2 Results

Experimental results for the $CaCO_3$ system have been summarized in Table 4-1. The reported precipitation rates for these experiments are based on the total calcium material balance as derived in Section 4-1. The relative saturations were calculated using the chemical equilibrium computer program as described earlier. The precipitation rate for $CaCO_3$ (in mMoles/gram-min) is plotted versus solution relative saturation in Figure 4-1.

4.3 Discussion of Results

Previous investigators have developed the concept of a metastable region of growth for many crystal systems. This region is bounded by the equilibrium solubility product curve for the particular precipitating species and a certain level of supersaturation below which normal crystal growth will occur but additional nuclei will not form. Since initiation of scaling required nucleation, it is important to define the limits of this metastable region for the $CaCO_3$ system.

From Figure 4-1, it is clear that the mechanism of $CaCO_3$ crystal growth undergoes a radical change for solution relative saturations greater than approximately 2.5. This abrupt change in the $CaCO_3$ rate curve is attributed to an incipient nucleation process in addition to normal crystal growth.

Photomicrographs comparing $CaCO_3$ seed crystals with product crystals were used to detect the degree of formation of new crystals or the onset of nuclei production during the kinetic runs. These photographs suggested that the rapid rise in the $CaCO_3$ precipitation rate at relative saturations greater than 2.5 is due to nucleation.

TABLE 4-1. EXPERIMENTAL DATA - PRECIPITATION KINETICS OF $CaCO_3$

Run #	Amount of Seed (g)	Feed Flow Rate		Feed Concentration		Reactor Temp. (°C)	Reactor pH	Steady State Effluent Conc.		Relative Saturation	Precipitation Rate (mMole/g-min)
		$CaCl_2$ (ml/min)	Na_2CO_3 (ml/min)	$CaCl_2$ (mMole/l)	Na_2CO_3 (mMole/l)			Calcium (mMole/l)	Carbonate (mMole/l)	$\frac{a_{Ca^{+2}} \cdot a_{CO_3^{-2}}}{Ksp}$	
1	10.00	100	100	0.750	1.010	30.00	9.61	0.155	0.207	1.584	.0044
2	10.00	75	75	1.400	1.325	30.00	9.60	0.276	0.355	2.090	.0064
3	10.00	100	100	1.400	1.161	30.00	9.58	0.246	0.293	2.215	.0091
4	10.00	"	"	1.390	1.480	30.00	9.84	0.187	0.304	2.600	.0102
5	10.00	"	"	1.480	1.555	30.00	9.84	0.180	0.300	2.468	.0112
6	10.00	"	"	1.560	1.665	30.00	9.85	0.182	0.327	2.686	.0120
7	10.00	"	"	2.930	2.815	30.30	9.84	0.163	0.389	2.617	.0260
8	10.00	"	"	2.000	2.010	30.10	10.42	0.104	0.311	2.536	.0179
9	10.00	"	"	0.767	0.795	30.20	11.11	0.046	0.424	1.806	.0067
10	10.00	"	"	2.605	2.280	30.10	9.65	0.238	0.369	2.723	.0213
11	10.00	"	"	0.213	0.205	30.00	11.17	0.088	0.103	1.144	.0004

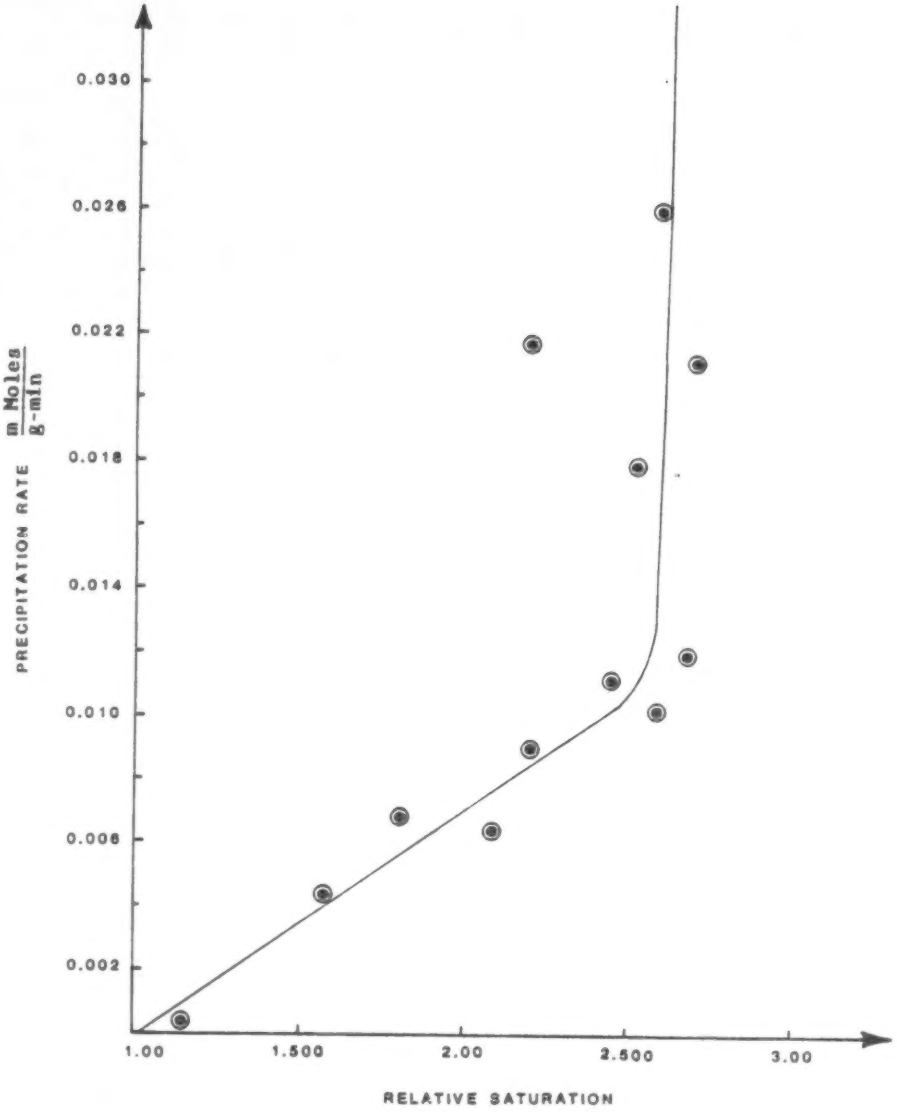

Figure 4-1. $CaCO_3$ precipitation kinetics. 02-1782-1

For supersaturations less than approximately 2.5, it is clear that qualitatively the linear driving force function appears to offer a good representation of the data. It is over this linear region that the limits of normal crystal growth for $CaCO_3$ are defined. That is, normal $CaCO_3$ crystal growth without nucleation is expected to occur in this linear metastable region.

4.4 Conclusions

From experimental measurements of $CaCO_3$ precipitation kinetics, we can state the following conclusions:

- A metastable crystal growth region bounded by a solution relative saturation of approximately 2.5 times the solubility product is observed. Below this level of supersaturation, precipitation occurs primarily on existing seed crystals. For solution supersaturations greater than approximately 2.5, nucleation begins to occur resulting in rapid acceleration of growth rates.

- The precipitation kinetics of $CaCO_3$ within the limits of the metastable growth region may be described by a rate expression of the form:

  $$R = \text{Rate (mMoles/min)} = k \cdot M \cdot (R.S.-1) \quad (4\text{-}4)$$

  where K (mMoles/gram-min) is the rate constant for the expression, M (grams) is the mass of seed crystals, and R.S. is the relative saturation defined by the ratio of the activity product to the solubility product for the precipitating species.

- The dependence of the rate on the amount of seed crystals present initially is not entirely clear. Experimental attempts to demonstrate the effect of the initial amount of seed on the rate did not provide a complete description of the seed-dependent term, M, in the rate expression.

5.0 EXPERIMENTAL RESULTS FOR $Mg(OH)_2$

This section presents the results of the experiments performed to determine $Mg(OH)_2$ precipitation kinetics. First, the method used for correlating the data is described. Then the actual data is presented in both tabular and graphical form and discussed.

5.1 Kinetics Data Processing

For the batch-solid kinetics experiments, a steady-state precipitation rate can be calculated from a straightforward material balance. Steady-state material balances may be written for the reactor in terms of either total magnesium or total hydroxide. That is:

$$(F_i \cdot C_i)_{inlet} - (F_i \cdot C_i)_{outlet} = R = \text{Precipitation Rate} \quad (5\text{-}1)$$

where F_i = flow rate in (ℓ/min),

C_i = concentration in (mMoles/ℓ),

R = rate of precipitation in (mMoles/min), and

i = magnesium or hydroxide.

Thus, equation 5-1 expresses the difference in the rate of material entering and leaving the reactor, and this difference is the rate at which solid material is produced in the reactor, or the rate of precipitation. This precipitation rate is calculated then by measuring the feed and effluent flow rates and determining the concentrations by analytical means for each kinetics experiment.

An additional check is provided by a total solids material balance. That is, the amount of product solids for a run is determined by emptying the reactor through the bottom port following shutdown so that the solids are retained on the filter membrane. After drying, the product cake is weighed and compared to the amount of seed material introduced initially. This mass difference is equal to the time integral of the experimental reaction rate multiplied by the $Mg(OH)_2$ molecular weight. This corresponds closely to the experimental steady-state precipitation rate multiplied by the total run time, since the reactor composition approaches steady-state in a short period of time compared to the total time duration of the run.

The $Mg(OH)_2$ precipitation rate, R, determined for a particular run in the above manner, is expressed as a function of the steady-state solution relative saturation. The relative saturation is defined as the ratio of the reactor solution activity product for the precipitating species, in this case, $a_{Mg^{+2}} \cdot a^2_{OH^-}$, to the equilibrium solubility product, Ksp, for $Mg(OH)_2$. Activities for the particular solution species are calculated by inputting pertinent reactor solution information, such as concentrations of magnesium, chloride and sodium, pH, and temperature, to the chemical equilibrium computer program. Reactor solution relative saturations are controlled experimentally by varying the mean reactor residence time or the inlet feed compositions from run to run.

A suitable rate expression for $Mg(OH)_2$ solid precipitation from supersaturated liquor may be written in the following form:

$$R = k \cdot M \cdot \phi \qquad (5\text{-}2)$$

where R = rate of solid precipitation,

k = rate constant, which may vary with liquor temperature, composition, and transport parameters,

ϕ = driving force term related to the degree of $Mg(OH)_2$ supersaturation,

M = term dependent on the amount of solid phase present.

The term, M, is usually assumed to be proportional to the exposed surface area of the solid phase. This is obviously difficult to quantify in experiments with suspensions of many fine particles of seed crystals; therefore, no crystal surface area measurements were attempted. Normally, as in this case of $Mg(OH)_2$ precipitation kinetics, the term is equated to the mass of initial seed crystals and therefore has the units of "grams."

For dissolution and precipitation reactions, ϕ, the driving force team, is normally taken to be the difference between the actual and equilibrium quantities of the reacting species, perhaps raised to some power. If one assumes a linear dependence of precipitation rate on the driving force function, then equation 5-2 can be written as:

$$R(\text{mMoles/min}) = k(\text{mMoles/gram-min}) \cdot M(\text{grams}) \cdot (\text{R.S.}-1) \quad (5\text{-}3)$$

where R.S. is the solution relative saturation as defined earlier. In this study, the precipitation rate divided by the mass of seed crystals (10.0 grams) is analyzed in terms of the solution relative saturation.

5.2 Results

Experimental results for the $Mg(OH)_2$ system have been summarized in Table 5-1. The reported precipitation rates for these experiments are based on the average of the total magnesium and total hydroxide material balances as derived in Section 3.1. The relative saturations were calculated using the chemical equilibrium computer program as described earlier. The precipitation rate for $Mg(OH)_2$ (in mMoles/gram-min) is plotted versus solution relative saturation in Figure 5-1.

5.3 Discussion of Results

Previous investigators have developed the concept of a metastable region of growth for many crystal systems. This region is bounded by the equilibrium solubility product curve for the particular precipitating species and a certain level of supersaturation below which normal crystal growth will occur but additional nuclei will not form. Since initiation of scaling requires nucleation, it is important to define the limits of this metastable region for the $Mg(OH)_2$ system.

From Figure 5-1, it is clear that the mechanism of $Mg(OH)_2$ crystal growth undergoes a radical change for solution relative saturations greater than approximately 3.4. This abrupt change in the $Mg(OH)_2$ rate curve is attributed to an incipient nucleation process in addition to normal crystal growth.

Photomicrographs of the $Mg(OH)_2$ seed material were compared with product material from runs at low and high solution relative saturations. The occurrence of nucleation at high solution relative saturation could not be determined from these representative photomicrographs due to the characteristic small size ($\leq 1.0\mu$) of the $Mg(OH)_2$ product crystals. Photomicrographs of the crystals at higher resolution could not be obtained.

TABLE 5-1 EXPERIMENTAL DATA-PRECIPITATION KINETICS OF $Mg(OH)_2$

Run #	Amount of Seed (gm)	Feed Flow Rate		Feed Concentration		Reactor Temp. (°C)	Reactor pH	Steady State Effluent Conc.		Relative Saturation	Precipitation Rate (mMole/gm-min)
		MgCl (ml/min)	NaOH (ml/min)	$MgCl_2$ (mMole/l)	NaOH (mMole/l)			Magnesium (mMole/l)	Hydroxide (mMole/l)	$\frac{a_{Mg^{+2}} \cdot a^2_{OH^-}}{Ksp}$	
1	10.0	75.0	75.0	0.613	1.190	30.0	10.42	0.217	0.402	2.072	0.00128
2	10.00	75.0	75.0	1.340	2.940	29.9	10.51	0.257	0.497	3.425	0.00645
3	10.00	75.0	75.0	1.740	2.875	30.0	10.42	0.3075	0.409	2.794	0.00818
4	10.00	75.0	75.0	2.215	3.665	30.0	10.44	0.350	0.430	3.404	0.01133
5	10.00	75.0	75.0	0.896	1.795	30.0	10.50	0.254	0.487	3.356	0.00292
6	10.00	75.0	75.0	0.692	1.485	30.0	10.50	0.191	0.512	2.574	0.00200
7	10.00	75.0	75.0	0.713	1.425	30.0	10.50	0.171	0.509	2.295	0.00215
8	10.00	75.0	75.0	0.452	0.871	30.0	10.45	0.155	0.450	1.707	0.00068

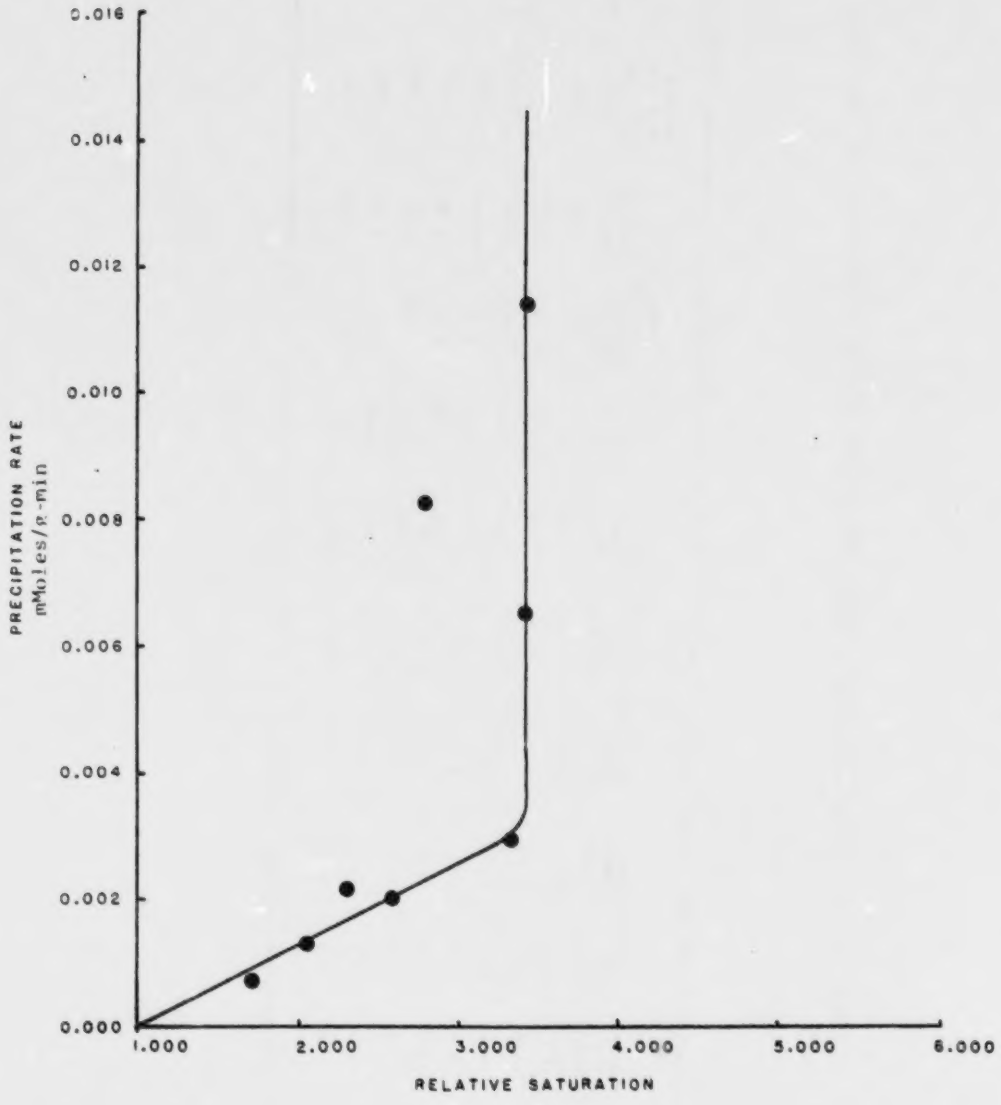

Figure 5-1. $Mg(OH)_2$ precipitation kinetics.

For supersaturations less than approximately 3.4, it is clear that qualitatively the linear driving force function appears to offer a good representation of the data. It is over this linear region that the limits of normal crystal growth for $Mg(OH)_2$ are defined. That is, normal $Mg(OH)_2$ crystal growth without nucleation is expected to occur in this linear metastable region.

5.4 Conclusions

From experimental measurements of $Mg(OH)_2$ precipitation kinetics, we can state the following conclusions.

- A metastable crystal growth region bounded by a solution relative saturation of approximately 3.4 times the solubility product is observed. Below this level of supersaturation, precipitation occurs primarily on existing seed crystals. For solution supersaturations greater than approximately 3.4, nucleation begins to occur resulting in rapid acceleration of growth rates.

- The precipitation kinetics of $Mg(OH)_2$ within the limits of the metastable growth region may be described by a rate of expression of the form:

  $$R = \text{Rate (mMoles/min)} = k \cdot M \cdot (R.S. - 1) \qquad (5\text{-}4)$$

  where k (mMoles/gram-min) is the rate constant for the expression, M (grams) is the mass of seed crystals, and R.S. is the relative saturation defined by the ratio of the activity product to the solubility product for the precipitating species.

- The dependence of the rate on the amount of seed crystals present initially is not entirely clear. Experimental attempts to demonstrate the effect of the initial amount of seed on the rate did not provide a complete description of the seed-dependent term, M, in the rate expression.

Appendix D. Ash Characterization for Colstrip and Montour Fly Ashes

1.0 INTRODUCTION

Five power plants have been selected for study representing typical situations in major geographical regions of the United States. These five plants are: 1) Four Corners, Arizona Public Service Co.; 2) Bowen, Georgia Power Co.; 3) Comanche, Public Service Co. of Colorado; 4) Montour, Pennsylvania Power and Light Co.; and 5) Colstrip, Montana Power Co. This appendix describes the results of bench-scale sluicing tests performed with fly ash from the last two plants. The results of similar studies performed on the ash from the first three plants are presented in the final report for EPA Contract No. 68-02-1319, "Ash Characterization Studies", which was performed in support of this program (see Appendix L).

1.1 Background

Recent emphasis on water recycle/reuse in the electric power industry has induced utilities to investigate the feasibility of recycling water which has been used to sluice coal ash. This system is known as a closed-loop ash sluicing facility. The engineering involved in designing such a facility necessitates the prediction of scaling potentials of $CaCO_3$, $Mg(OH)_2$ and $CaSO_4 \cdot 2H_2O$ so that the system can be designed to control possible scaling problems. To predict scaling potentials for these species, the dissolution characteristics of the coal ash must be known. Therefore, it is important to investigate the ash dissolution characteristics which will be involved in such an ash handling facility. A bench-scale, closed-loop ash sluicing facility was built to study the dissolution characteristics of the ash in a system of this type. Measurements were made to determine the chemical composition of the water at various locations in the system. The values obtained will aid in the prediction of scaling potentials for $CaCO_3$, $Mg(OH)_2$ and $CaSO_4 \cdot 2H_2O$ in closed-loop ash sluicing facilities.

1.2 Summary

Six experiments were performed using fly ash supplied by PP&L and MPC. The first three were performed with ash from the PP&L Montour Steam-Electric Station. The last three were performed with ash from the MPC Corette Steam-Electric Station as a substitute for fly ash from the Colstrip Steam-Electric Station, which was not available because of the wet scrubbing employed at Colstrip.

The first experiment was performed with the fly ash being sluiced near 10% solids in a recycle system for about 50 hours. The pond recycle water comprised 84% of the sluice water and simulated 2 cycle cooling tower blowdown was used as makeup. The second experiment was performed with a 7% slurry in the mix tank in a recycle system for about 30 hours. The recycled water comprised 88% of the sluice water and the makeup water was of similar composition as was used in the first experiment. The third experiment was performed under the same conditions as those used in the second except the makeup water simulated 8 cycle cooling tower blowdown from the Montour cooling towers.

From these experiments it was learned that the reactivity of this ash was less under these more realistic conditions than was measured in batch dissolution studies using deionized water. The reactivity of the ash is an important parameter in determining the scaling potential of the slurry in a wet ash sluicing system. These experiments also point out that this ash does have the potential to be sluiced in a recirculating system without significant scale formation.

The last three experiments were performed with MPC ash, and two cycle simulated cooling tower blowdown from the Montour Station. Simulated Montour blowdown was used so that a comparison of ash reactivity between plants could be made and so the effects of makeup water composition could be investigated. The first two experiments performed with this ash were done for 30 hours with an 89% recycle, and about 7% solids in the slurry. Carbon dioxide was bubbled into the ash pond in the second experiment to simulate CO_2 transfer from the air to the pond. The third experiment was performed on a once-through basis with the same water quality used as makeup in the first two experiments.

These experiments showed that different ashes can display great differences in reactitivity under similar conditions. The MPC ash was much more alkaline producing pH's near 12 in the mix tank as compared to the more neutral pH's experienced with the PP&L ash. The reactivity of the MPC ash was much less under these experimental conditions than was found under batch dissolution studies using deionized water.

These six experiments display more than anything that ash sluicing system design must take into account a large number of interacting factors. The reactivity of the ash is dependent on the water quality of the sluice which is dependent upon the percent recycle, the quality of the makeup and finally the reactivity of the ash.

2.0 EXPERIMENTAL

In this section a description of the six experiments performed is presented. A description of the equipment used is presented initially, along with the general approach used. This is followed by a detailed description of the three experiments performed with the fly ash from the Pennsylvania Power and Light Montour Station. Finally, the three experiments performed with the fly ash supplied by Montana Power Co. are described.

2.1 Technical Approach

A depiction of the laboratory scale ash sluicing facility which was built to simulate a closed-loop ash handling system is shown in Figure 2-1. Water from the settling pond was pumped to the mixing tank, a 6-liter (1.6 gal) Plexiglass cylinder where the coal ash was mixed with the sluice water. The slurry formed was allowed to flow by gravity from the mixing tank to the settling pond. The settling pond was constructed of fiberglass and had a capacity of 454ℓ (120 gal). The method of gravity flow from the mixing tank to the settling pond was adopted because dissolution occurs quickly in the mixing tank. Therefore, the majority of dissolution occurs in the mixing tank with only a minor fraction occurring in other portions of the system. Batch dissolution studies indicate that the major portion of the dissolution of the ash occurs within 15 minutes and the mixing tank has a residence time of over 20 minutes.

Makeup water was fed into the mixing tank to replenish water that was occluded with the sludge in the pond at 40 weight percent solids. The chemical composition of this liquor varied among runs to simulate the composition of actual makeup water streams from the power plants studied (Montour and Colstrip). The major portion of the sluice water was made up of pond water recycled to the mixing tank.

The makeup water and the recycle were pumped with peristaltic pumps. Rotometers were used to monitor flow rates. The fly ash was fed into the mixing tank by a Model SCR-20 precision volumetric screw feeder manufactured by Vibra Screw, Inc.

The liquor chemical compositions of the system must be determined at steady state for values which can be effectively used in a computer model of a closed-loop ash sluicing facility. For the system to be at steady state, the chemical

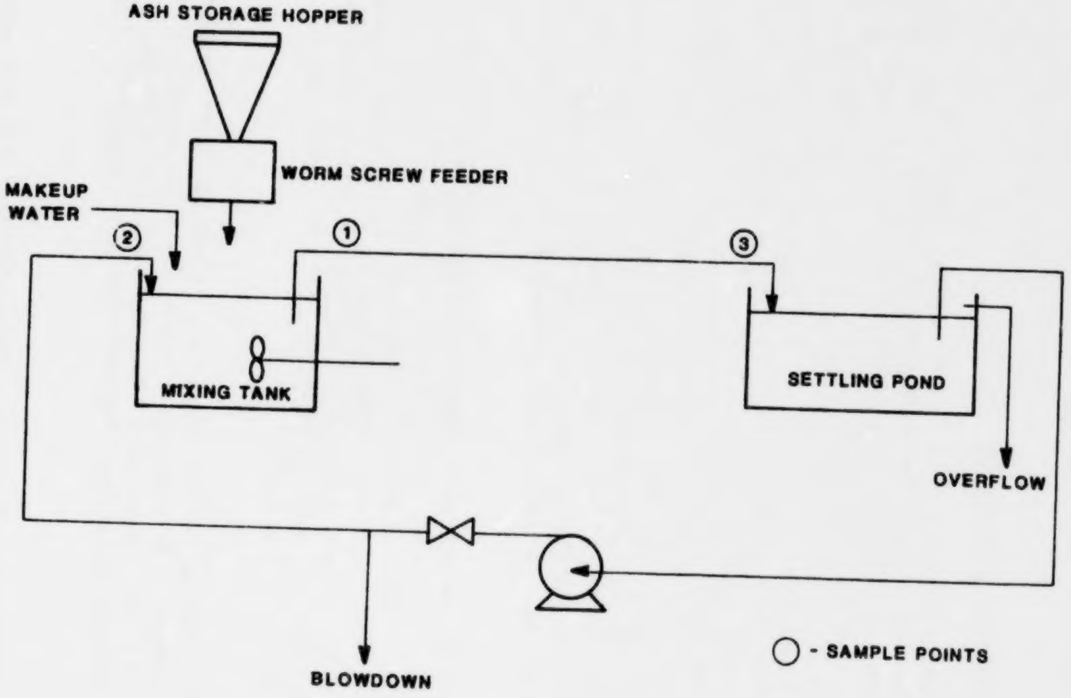

Figure 2-1. Bench-scale simulation model of ash pond facilities.

composition of the liquor entering the mixing tank from the settling pond must be constant, and the chemical composition of the liquid flowing from the mixing tank to the settling pond must be constant. The equation

$$y = (y_o - y_i)e^{-t/\tau} + y_i \qquad (2\text{-}1)$$

describes the system surrounding the settling pond assuming no reaction occurs, where y is the concentration of the pond overflow, y_o is the initial pond overflow concentration, y_i is the inlet concentration to the pond, t is the number of hours the experiment is run, and τ is the residence time of the settling pond. This equation may be used to make a rough estimate for the time necessary for the system to reach steady state.

The residence time in the pond was determined by the volume of the pond liquor above the sludge. The amount of liquid in the pond was measured at the beginning and the end of each experiment. The average was used to calculate τ. All experiments were performed for about five pond residence times (τ). At least three residence times will probably be necessary to achieve steady state since the incoming stream of the settling pond is not constant as it is affected by the outgoing stream of the settling pond and precipitation and/or dissolution will be occurring in the system.

Samples were collected at regular intervals. These samples were filtered and diluted at the time of collection. Ion chromatography was used to measure calcium, magnesium, sodium, total sulfate, chloride, and nitrate. This method was used since it is generally faster than conventional methods and the timing of these experiments was critical in completing the project (DI-170). Carbonate samples were collected separately and were preserved in a NH_4OH-EDTA buffer system. The pH measurements were taken immediately.

The fly ash used for the first three experiments was obtained directly from the electrostatic precipitator at Pennsylvania Power and Light's Montour Station. The fly ash used for the last three experiments was obtained from the Montana Power Co. J. E. Corette plant. The ash from the Colstrip plant could not be obtained in the dry form because of the SO_2 scrubber in the plant's exhaust system. The coal used in the Corette plant comes from the same mine and the fly ash from Corette was obtained dry.

2.2 Montour SES

In Table 2-1 the operating conditions for the three experiments performed with the ash supplied by Pennsylvania Power & Light (PP&L) is presented. The feed rates of the three streams that flow into the mixing tank are shown as well as the residence time in both the tank and the pond at these flow rates. The mixing tank has a volume of 6 liters, and the average volume of the liquor above the sludge in the pond was used to calculate the pond residence time.

The first experiment was carried out for about 50 hours to insure steady state operation. Because preliminary results from this experiment indicated that a shorter period of operation would also attain steady state, the second two experiments were only performed over a 30 hour period. The volume of the liquor in the pond did increase slightly over the time span of the experiments. Since the first experiment was performed over a much longer period the average volume of the pond liquor was correspondingly larger.

The flow rate of the sluice water (makeup + recycle) was the same for all three experiments. The ash feed rate and the makeup water flow rate were larger in the first experiment than in the other two. This caused the percent solids in the slurry to be greater in the first experiment. The values reported in Table 2-1 are the average measured values over the length of the experiment. The makeup was calculated to be equal to the amount of water that would be occluded with the sludge in the pond at 40 weight percent solids.

Table 2-2 presents the composition of the makeup waters used in these three experiments. These are measured values that were obtained from sample analyses. The water in the first two experiments was made to approximate cooling tower blowdown from the Montour cooling towers at two cycles of concentration. The water for the third experiment was made to simulate eight cycle cooling tower blowdown from Montour.

The initial conditions of the pond water in each experiment are shown in Table 2-3. The concentrations were measured in the same manner that was used to measure the makeup water. In the first two experiments the initial charge of pond water was approximately the same as the makeup water. In the third experiment the pond water from the second experiment was used initially.

TABLE 2-1. EXPERIMENTAL CONDITIONS (MONTOUR)

	Experiment 1	Experiment 2	Experiment 3
Ash Feed Rate to Mixing Tank, g/min	30	22	22
Makeup Water Rate to Mixing Tank, mℓ/min	45	35	35
Recycle from Pond to Mixing Tank, mℓ/min	245	255	255
Percent Solids in Slurry	10%	7%	7%
Mixing Tank Residence Time, hrs	.345	.345	.345
Pond Residence Time, hrs	6.8	6.1	6.1
Duration of Experiment, Experiment, hrs	49	29.5	30

TABLE 2-2. MAKEUP WATER COMPOSITION (MONTOUR)

	Experiment 1	Experiment 2	Experiment 3
Chloride (mg/ℓ)	65.0	71.0	195.0
Sulfate (mg/ℓ)	129.0	131.0	416.0
Nitrate (mg/ℓ)	11.2	18.6	36.0
Sodium (mg/ℓ)	17.7	12.7	57.5
Calcium (mg/ℓ)	51.3	46.9	174.0
Magnesium (mg/ℓ)	14.1	6.6	36.5
Carbonate (mg/ℓ)	14.1	17.9	23.5

TABLE 2-3. INITIAL POND WATER (MONTOUR)

	Experiment 1	Experiment 2	Experiment 3
Chloride (mg/ℓ)	109.0	73.5	49.7
Sulfate (mg/ℓ)	163.0	132.0	1680.0
Nitrate (mg/ℓ)	15.5	10.5	6.8
Sodium (mg/ℓ)	22.1	12.9	85.1
Calcium (mg/ℓ)	63.0	52.1	613.0
Magnesium (mg/ℓ)	16.5	7.5	24.2
Carbonate (mg/ℓ)	26.6	17.2	12.6
Volume, liters	80.0	80.0	80.0

In summary, the first experiment was performed for 50 hours, with a larger percent solids in the slurry than was used in the other two experiments. The makeup water and the initial pond water approximated the water quality found in two cycle cooling tower blowdown at Montour. The second experiment was performed with similar makeup and pond water compositions, but with a lower ash feed rate, causing the slurry to have a lower percent solids. The third experiment was performed with 8 cycle cooling tower blowdown and the residual pond water from the second experiment. The other operating conditions for the third experiment were the same as those used in the second run.

2.3 Colstrip SES

In Table 2-4 the operating conditions for the three experiments performed with the ash supplied by Montana Power Company (MPC) is presented. The feed rates of the streams that flow into the mixing tank are shown along with the residence times of the pond and the tank at these flow rates. The mixing tanks and the pond residence times were calculated in the same manner that was done for the Montour experiments.

The first two experiments were performed under recycle conditions for about 30 hours. The operating conditions were exactly the same for both runs except that CO_2 was bubbled into the pond in the second experiment in order to keep the pH of the pond liquor near 7.5. This was done in order to study the effect that CO_2 transfer in the pond had on the recirculating system.

The third experiment was performed to simulate a once-through ash sluicing operation. The percent solids in the slurry was increased because the total water flow was decreased and the ash feed rate was not changed. This was done in order to see if a slurry of this ash near 10% solids could be sluiced without scale formation. The pond water was contacted with CO_2 in order to maintain a pH near 7.7.

Table 2-5 presents the composition of the makeup water used for these three experiments. These are measured values that were obtained using sample analyses. The water used for all three experiments simulated two cycle cooling tower blowdown from the Montour station. This was done because ash sluicing is performed as part of the SO_2 scrubbing at Colstrip and there wasn't any representative stream composition from Colstrip to use as makeup. The use of the Montour water allowed comparison of the different ashes with similar makeup water composition.

TABLE 2-4. EXPERIMENTAL CONDITIONS (COLSTRIP)

	Experiment 1	Experiment 2	Experiment 3
Ash Feed Rate to Mixing Tank, gm/min	15	15	15
Makeup Water Rate to Mixing Tank, mℓ/min	30	30	150
Recycle from Pond to Mixing Tank, mℓ/min	255	255	0
Mixing Tank Residence Time, hrs	0.35	0.35	0.66
Pond Residence Time, hrs	6.1	6.1	--
Duration of Experiment, hrs	30.5	30	8

TABLE 2-5. MAKEUP WATER COMPOSITION (COLSTRIP)

	Experiment 1	Experiment 2	Experiment 3
Chloride (mg/ℓ)	32.0	32.0	28.8
Sulfate (mg/ℓ)	115.0	75.8	115.0
Nitrate (mg/ℓ)	11.2	11.2	10.5
Sodium (mg/ℓ)	15.2	11.0	11.5
Calcium (mg/ℓ)	60.2	48.1	52.1
Magnesium (mg/ℓ)	12.4	11.7	19.4
Carbonate (mg/ℓ)	9.5	12.8	13.7

The initial pond water composition for each experiment is presented in Table 2-6. For the first experiment the pond was filled with 80 liters of the makeup water. For the second and third experiments 80 liters of the pond water left from the previous experiment were used as the initial pond water.

TABLE 2-6. INITIAL POND WATER (COLSTRIP)

	Experiment 1	Experiment 2	Experiment 3
Chloride (mg/ℓ)	32.0	39.1	31.2
Sulfate (mg/ℓ)	115.0	576.0	566.0
Nitrate (mg/ℓ)	11.2	10.5	12.4
Sodium (mg/ℓ)	15.2	21.9	52.9
Calcium (mg/ℓ)	60.2	882.0	481.0
Magnesium (mg/ℓ)	12.4	0.0	0.0
Carbonate (mg/ℓ)	9.5	81.6	655.0
Volume, liters	80.0	80.0	80.0

In summary, three experiments were performed with ash similar to that produced at Colstrip. The first employed recycle without CO_2 transfer in the pond. The second was operated under identical conditions as were used in the first experiment except CO_2 was bubbled into the pond water. The third experiment was a once-through operation using higher percent solids in the slurry than was used in the previous two experiments.

3.0 RESULTS

In this section the results of all six ash sluicing experiments are presented. This includes information on the water quality in the mix tank and the pond under steady-state conditions. Mass balances were performed around the mix tank and net dissolution rates of the leachable species were calculated. The results of the studies performed with the ash supplied by PP&L are presented first followed by the results of the studies with the MPC ash.

3.1 Montour

First the justification for steady-state operation is presented using the results of Experiment 1. Then the final samples are presented and the potential for scale formation is looked at. The net dissolution rates in the mix tank and the reactivities of the ash are compared for the three experiments. Finally, the relevant conclusions concerning the results of these experiments are drawn.

3.1.1 Steady-State Operation

The first experiment performed with the PP&L ash was run for 50 hours to insure steady-state operation. Figures 3-1 through 3-7 present the concentration of the different key species in the pond water as a function of time. The first four graphs deal with the major species that were leached from the ash: sodium, calcium, sulfate, and magnesium. The other graphs deal with three other species which are not normally leached from fly ash to any significant degree: chloride, nitrate, and carbonate.

Figures 3-1, 3-2, and 3-3 include curves that were fit to the data using Equation 3-1:

$$y = (y_o - y_i)e^{-t/\tau} + y_i \qquad (3\text{-}1)$$

The parameters y_o and y_i were determined by plotting y versus $e^{-t/\tau}$, where τ = residence time of the pond (6.8 hours), and calculating the slope and the y-intercept using a linear least square regression. The results of these regressions are presented in Table 3-1. The values obtained for y_o and y_i obtained from the transformed plots (y versus $e^{-t/\tau}$) were then used to calculate the curves presented in the original plots (y versus t).

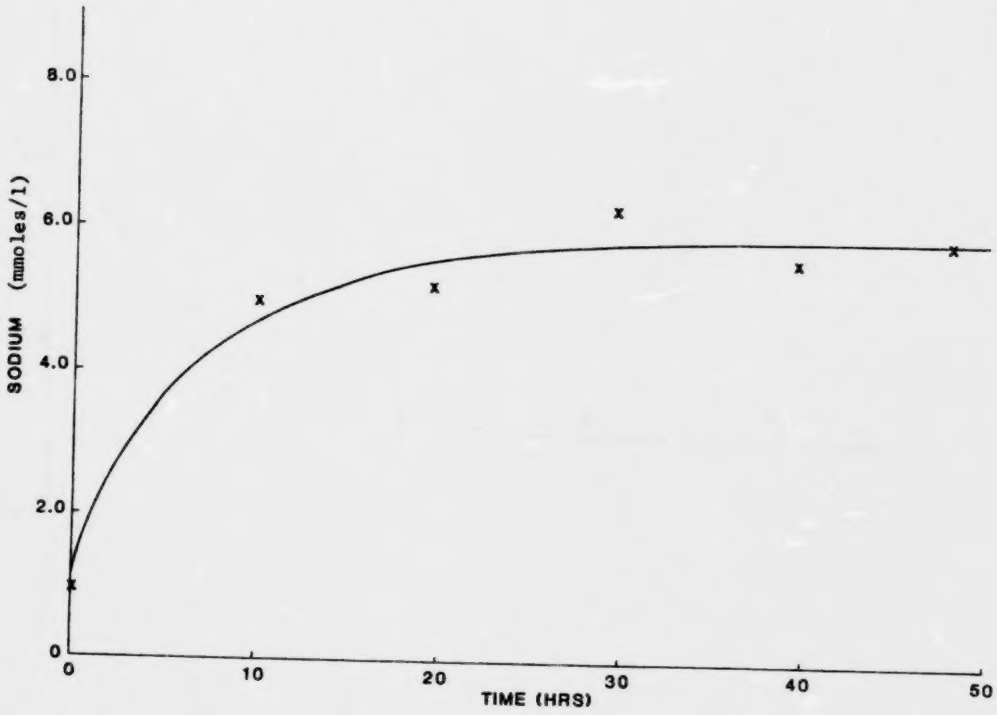

Figure 3-1. Sodium concentration in the pond vs. time.

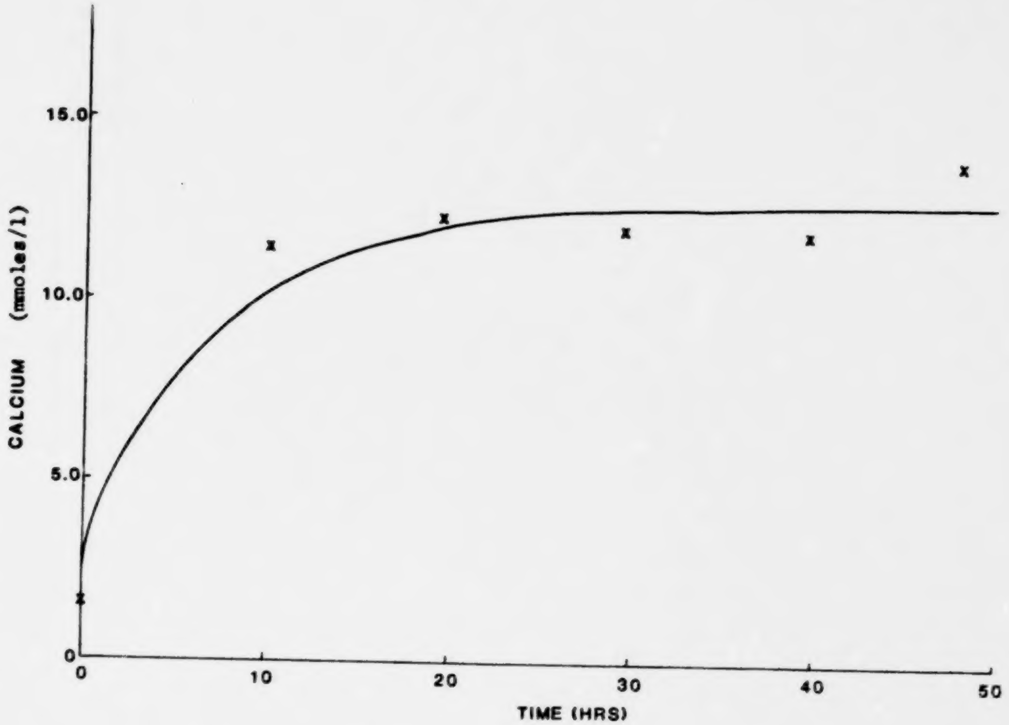

Figure 3-2. Calcium concentration in the pond vs. time.

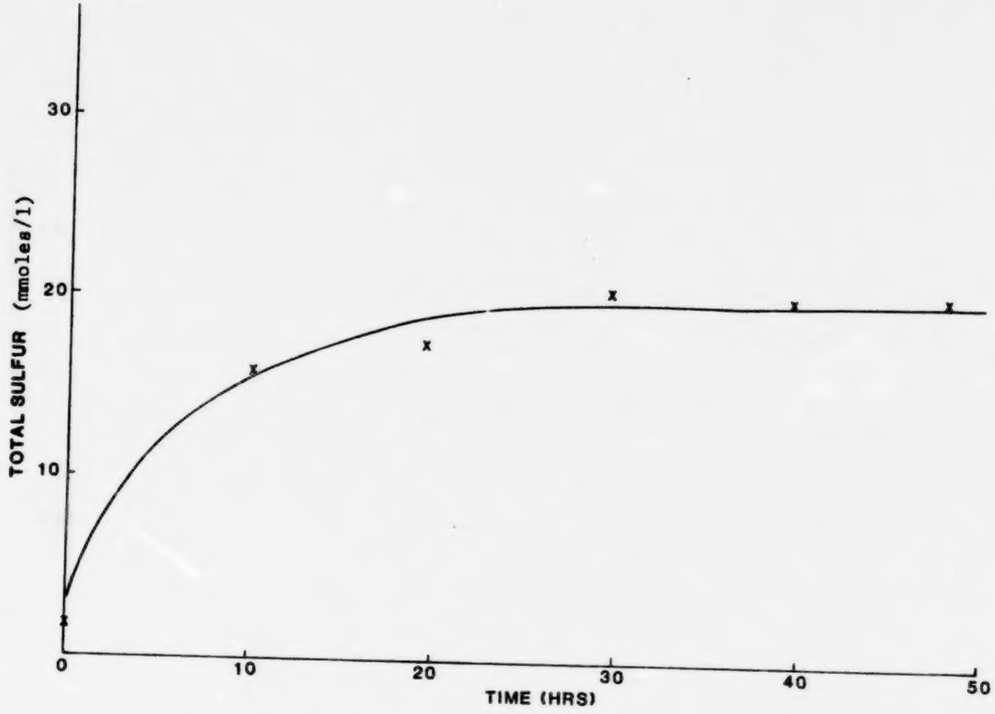

Figure 3-3. Sulfur concentration in the pond vs. time.

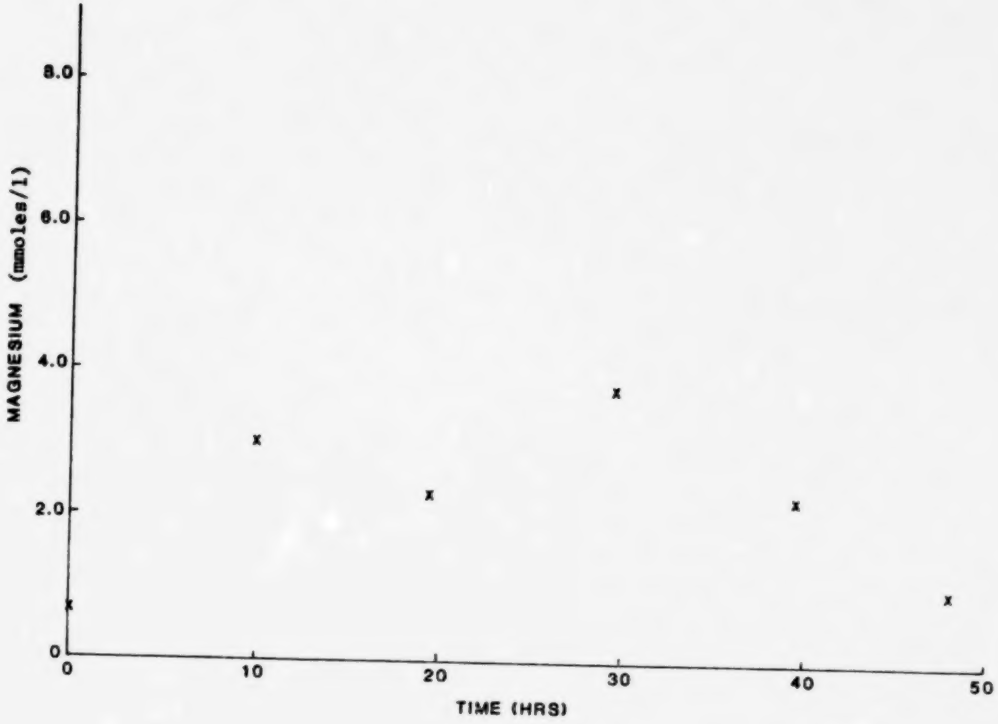

Figure 3-4. Magnesium concentration in the pond vs. time.

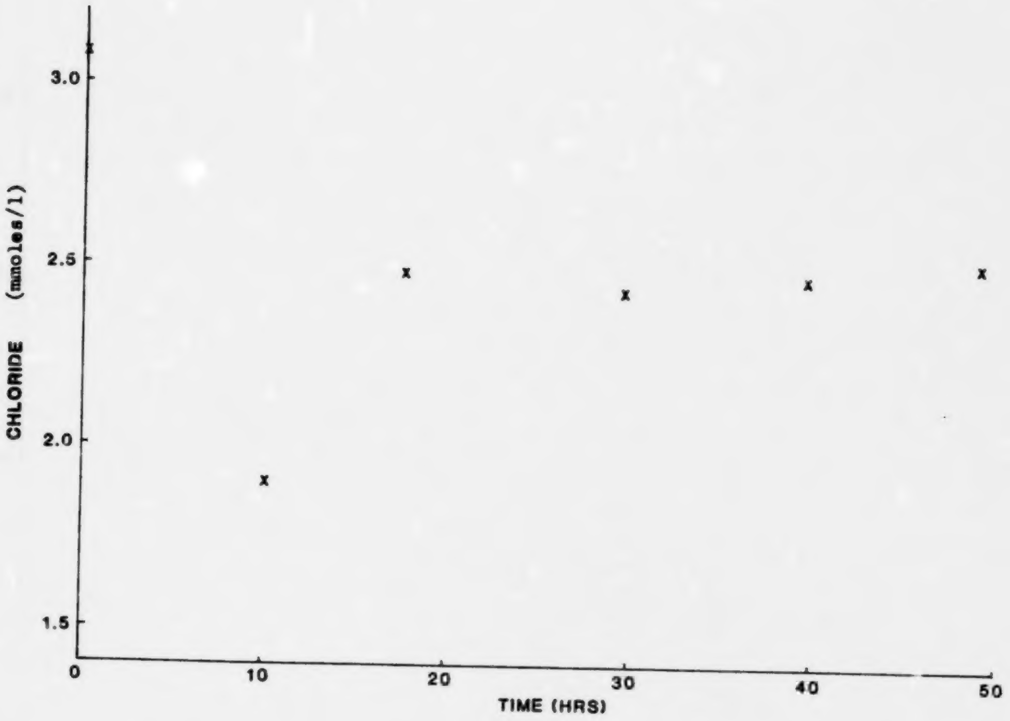

Figure 3-5. Chloride concentration in the pond vs. time.

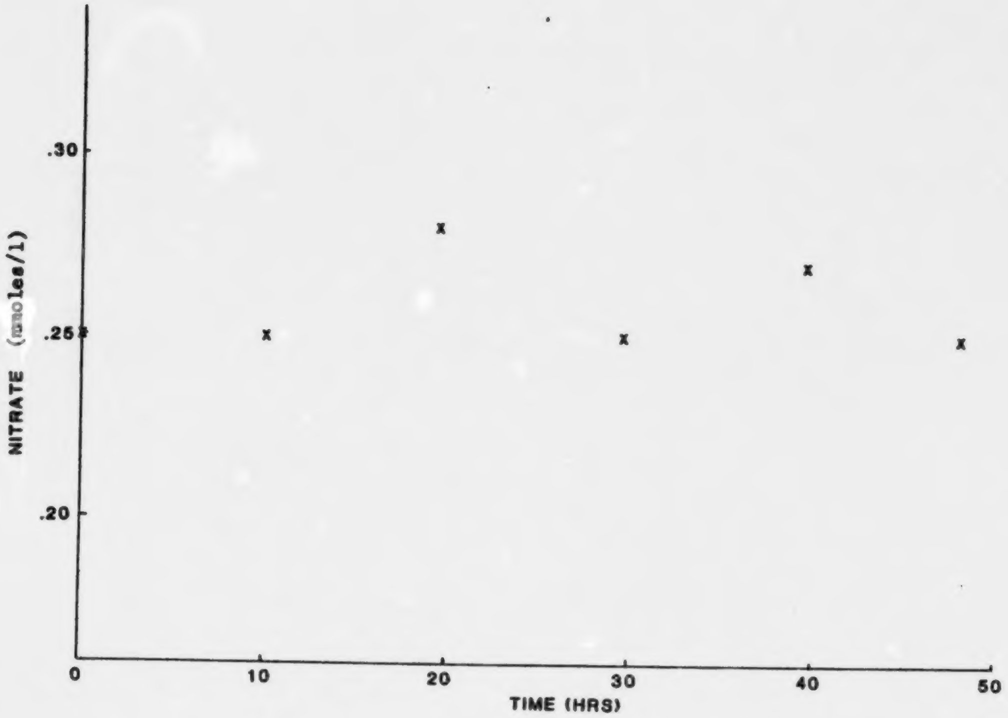

Figure 3-6. Nitrate concentration in the pond vs. time.

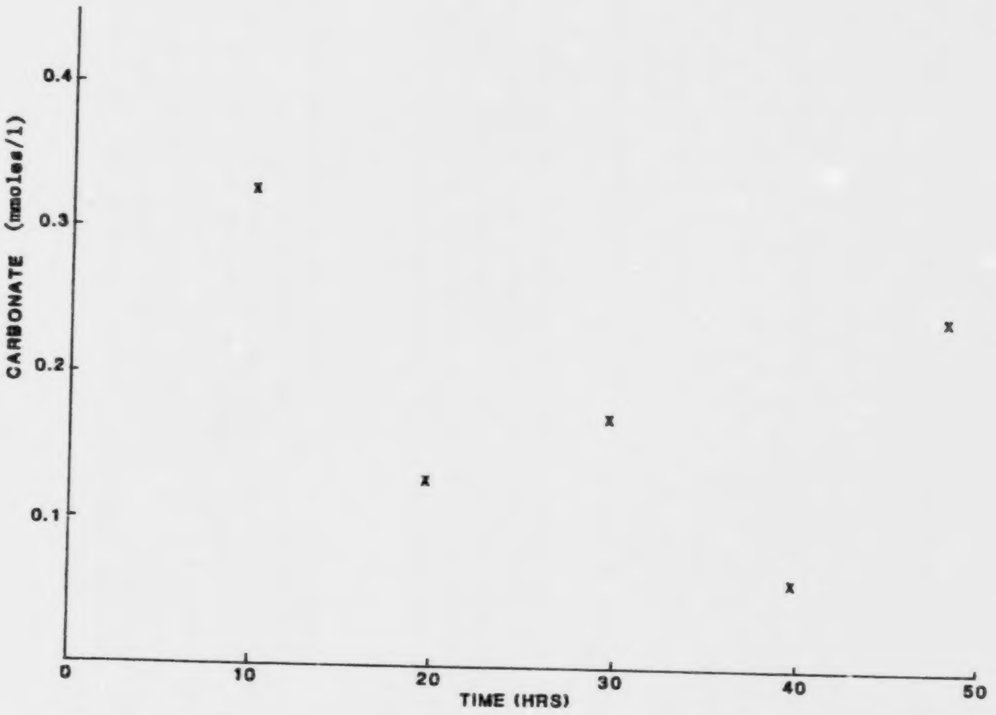

Figure 3-7. Carbonate concentration in the pond vs. time.

TABLE 3-1. MONTOUR EXPERIMENT 1 REGRESSION RESULTS

	slope $(y_o - y_i)$	y-intercept (y_i)	(y_o)	Coefficient of Determination (r^2)
Figure 3-1 (Sodium)	- 4.89	5.89	.996	.97
Figure 3-2 (Calcium)	-10.9	12.7	1.85	.97
Figure 3-3 (Sulfate)	-18.3	19.9	1.66	.99

These plots indicate that steady-state operation was attained in the system with respect to sodium, calcium, and sulfate concentration. They also point out that after 30 hours, about 4½ residence times, the system did not change significantly, justifying the shorter (30 hours) operating period for the other experiments.

Figure 3-4 is a plot of magnesium concentration in the pond as a function of time. Although it is a leachable species, the magnesium did not act as well behaved as the other leachable species. The large, somewhat random variation in concentration indicates that it did not reach steady state. Figures 3-5, 3-6, and 3-7 are plots of the non-leachable species in the pond as a function of time. The variation noted in these plots is most probably due to sampling error caused by incomplete mixing in the pond.

3.1.2 Chemical Analyses

For each experiment the results of the chemical analyses from the final samples were input into the equilibrium program. The program then calculated the relative saturations of $CaCO_3$ and $CaSO_4$. The relative saturation is a measurement of the tendency of a particular solid to scale.

Table 3-2 presents the chemical analyses as well as the relative saturations calculated by the program. This table includes the samples taken in both the mix tank and the ash pond. These results show there was no tendency to form $CaCO_3$ scale in any of these experiments. The low relative saturation of $CaCO_3$ in these samples was expected since all of the samples are acidic. The relative saturation of $CaSO_4$ was near one in all of the above cases, but less than the critical scaling value of 1.3-1.4. The concentrations of both calcium and sulfate did not change significantly between the pond and the mix tank implying that $CaSO_4$ precipitation was not occurring to any detectable extent.

3.1.3 Mass Balances

For each experiment, mass balances were performed around the mix tank at different times in the experiment including the final samples. The difference between the amount of a given species entering the tank and the amount leaving was assumed to be leached from the ash. Table 3-3 presents the results of these calculations for all three experiments.

These results confirm that in all three cases chloride, nitrate, and carbonate were not leached from the ash. The size and the fact that negative as well as positive rates are observed indicate that the values represent measurement errors. The values reported for sodium, calcium, sulfur, and magnesium are significantly larger and positive. This indicates that these species were leached from the ash.

Using Equation 3-2, the weight percent of each species leached from the ash was calculated:

$$W = \frac{D \cdot MW}{F} \times 100 \qquad (3\text{-}2)$$

where W = weight percent of species leached from the ash,

D = net dissolution rate of species (mmoles/min),

F = feed rate of the ash (mg/min), and

MW = the molecular weight of the species (g/mole).

The results of these calculations are presented in Table 3-4.

TABLE 3-2. FINAL SAMPLE RESULTS (MONTOUR)

	Experiment 1	Experiment 2	Experiment 3
MIX TANK:			
Sodium, mg/ℓ	147.0	101.0	145.0
Calcium, mg/ℓ	465.0	614.0	690.0
Sulfate, mg/ℓ	2054.0	1843.0	1910.0
Magnesium, mg/ℓ	44.2	30.6	44.2
Chloride, mg/ℓ	83.8	76.7	94.1
Nitrate, mg/ℓ	17.4	15.5	19.8
Carbonate, mg/ℓ	3.0	8.4	3.6
Arsenic, mg/ℓ	0.148	0.120	0.195
pH	5.6	6.9	6.9
Relative Saturation,* $CaCO_3$	7.7×10^{-4}	2.5×10^{-2}	1.2×10^{-2}
Relative Saturation,* $CaSO_4 \cdot 2H_2O$	.93	1.10	1.20
POND:			
Sodium, mg/ℓ	136.0	85.1	138.0
Calcium, mg/ℓ	517.0	589.0	690.0
Sulfate, mg/ℓ	1950.0	1690.0	1900.0
Magnesium, mg/ℓ	24.3	26.7	43.7
Chloride, mg/ℓ	88.8	78.1	85.2
Nitrate, mg/ℓ	15.5	17.4	20.5
Carbonate, mg/ℓ	14.4	10.8	3.6
Arsenic, mg/ℓ	0.118	0.087	0.171
pH	6.0	6.9	6.9
Relative Saturation,* $CaCO_3$	2.0×10^{-3}	3.2×10^{-2}	1.3×10^{-2}
Relative Saturation,* $CaSO_4 \cdot 2H_2O$	1.0	1.03	1.19

* Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C).

TABLE 3-3. NET DISSOLUTION RATES FROM MONTOUR FLY ASH

Species	Experiment 1		Experiment 2	Experiment 3	
	(29.5 hrs)	(49 hrs)	(29.5 hrs)	(25 hrs)	(30 hrs)
Sodium, mmoles/min	.42	.38	.31	.22	.21
Calcium, mmoles/min	1.29	.15	.65	.33	.45
Sulfate, mmoles/min	1.00	1.17	1.03	.68	.57
Magnesium, mmoles/min	.51	.26	.09	.01	.01
Chloride, mmoles/min	.11	-.01	.01	-.01	-.03
Nitrate, mmoles/min	.02	.01	-.01	-.01	-.01
Carbonate, mmoles/min	-.02	-.05	-.02	-.01	-.01

TABLE 3-4. MONTOUR FLY ASH REACTIVITY

Species	Experiment 1	Experiment 2	Experiment 3
Sodium, wt. %	0.03	0.03	0.02
Calcium, wt. %	0.10	0.12	0.07
Sulfate, wt. %	0.35	0.45	0.27
Magnesium, wt. %	0.03	0.01	0.001

The differences in the values obtained for Experiment 1 and Experiment 2 can be attributed to the percent solids in the slurry. In Section 2.1, it is shown that these two experiments were operated very similarly except that the slurry was 10% solids in the first case and 7% solids in the second. The weight percent of the calcium and sulfate leached from the ash was less in the case with higher solids, but the same was not true for sodium and magnesium.

The differences between Experiment 2 and Experiment 3 was the quality of the makeup water. In Experiment 3 where the total dissolved solids were significantly higher in the makeup water, and, therefore, in the slurry water, the ash was less reactive. For all four species less was leached from the ash in the third experiment. This implies that the reactivity of this ash increases with the water quality of the leachate. This conclusion is further supported when the results of this study are compared to the results of batch dissolution studies performed with this ash, reported in Appendix K. In the batch dissolution studies, the reactivity of the PP&L ash were examined under deionized water at pH 6 and 8 and at 5% and 10% slurries. In every case, the reactivity of the ash was greater under deionized water than under the more realistic conditions employed in this study.

3.1.4 Conclusions

The results of the three experiments performed with the PP&L ash lead to the following conclusions:

1) Steady-state behavior occurs in the experimental equipment at the end of three pond residence times.

2) Under the conditions studied, 84 to 88% recycle and 7 to 10% solids, this ash can be sluiced without significant scale formation. $CaCO_3$ scale does not present a problem but the relative saturation of gypsum is near the critical range.

3) The reactivity of this ash is dependent on the percent slurry and the water quality of leachate. Increased dissolved solids tends to cause the reactivity of this ash to decrease.

3.2 Colstrip

Three experiments were performed with the Colstrip ash. The results of these three experiments are presented in this section. This includes the chemical analyses of the final samples, the relative saturations of $CaCO_3$ and $CaSO_4$ for these samples and the results of mass balances performed around the mix tank to determine the reactivity of the ash. Finally, general conclusions are drawn from the results presented.

3.2.1 Chemical Analyses

For each experiment the results of the chemical analyses from the final sample were input into the equilibrium program. The program then calculated the relative saturations of $CaCO_3$ and $CaSO_4$. The relative saturation is a measurement of the tendency of a particular solid to precipitate.

Table 3-5 presents the chemical analyses used as inputs to the computer program and the calculated relative saturations. Samples were taken from both the mix tank and the pond. These results indicate that $CaSO_4$ scale should not present a problem under these operating conditions. However, $CaCO_3$ scale seems to represent a real danger. In all three cases in both the mix tank and the pond, the relative saturation of $CaCO_3$ exceeded its critical scaling value of 2.5 (Appendix C).

The first experiment was performed without pH control allowing the pH to rise to 12.6. This very high pH caused the relative saturation of $CaCO_3$ to reach a high value in the mix tank where calcium was leached from the ash. In the pond, $CaCO_3$ precipitated causing the carbonate level to drop and decrease the relative saturation from 7.8 to 3.7. In the second experiment CO_2 was bubbled into the pond maintaining a lower pH but increasing the relative saturation in the mix tank and the pond relative to the first experiment. In the second experiment, the relative saturation in the pond fell relative to the tank even though the calcium level remained the same and the carbonate level increased, because the pH fell from 11.7 to 7.6.

In all three experiments, there was no detectable level of magnesium in the liquid phase. This occurred because the pH in the mix tank was always above 8. Therefore, any magnesium leached from the ash or coming in with the makeup water probably precipitated out in the form of $Mg(OH)_2$. In the last two experiments where the pond reached a pH of 7.6 no magnesium was detected most probably because once the $Mg(OH)_2$ solid was formed in the tank, it settled with the sludge in the pond, and did not redissolve.

3.2.2 Mass Balance

For each experiment mass balances were performed around the mix tank at different times in the experiment including the final samples. The difference between the amount of a given species entering the tank and the amount leaving was assumed to be leached from the ash. Table 3-6 presents the results of these calculations for all three experiments.

These results indicate that only calcium and sulfate had significant net dissolution rates. Magnesium was expected to be leached from this ash based on other studies (see Appendix K) but as explained earlier the very high pH's occurring in

TABLE 3-5. FINAL SAMPLE RESULTS (COLSTRIP)

	Experiment 1	Experiment 2	Experiment 3
MIX TANK:			
Sodium, mg/ℓ	27.6	25.3	3.9
Calcium, mg/ℓ	1000.0	441.0	922.0
Sulfate, mg/ℓ	691.0	614.0	451.0
Magnesium, mg/ℓ	0.0	0.0	0.0
Chloride, mg/ℓ	39.1	29.1	29.5
Nitrate, mg/ℓ	14.3	14.3	10.5
Carbonate, mg/ℓ	4.8	21.0	10.8
pH	12.6	11.7	12.8
Relative Saturation,* $CaCO_3$	7.79	31.8	16.9
Relative Saturation,* $CaSO_4 \cdot 2H_2O$	0.53	0.42	0.30
POND:			
Sodium, mg/ℓ	27.6	52.9	4.6
Calcium, mg/ℓ	1240.0	481.0	377.0
Sulfate, mg/ℓ	595.0	566.0	413.0
Magnesium, mg/ℓ	0.0	0.0	0.0
Chloride, mg/ℓ	39.1	31.2	29.5
Nitrate, mg/ℓ	14.3	12.4	9.9
Carbonate, mg/ℓ	2.4	654.0	1030.0
pH	12.6	7.6	7.6
Relative Saturation,* $CaCO_3$	3.67	12.6	13.9
Relative Saturation,* $CaSO_4 \cdot 2H_2O$	0.51	0.39	0.25

* Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C).

TABLE 3-6. NET DISSOLUTION RATES FROM COLSTRIP FLY ASH

Species	Experiment 1		Experiment 2		Experiment 3	
	(15.5 hrs)	(30.5 hrs)	(25 hrs)	(30 hrs)	(6 hrs)	(8 hrs)
Sodium, mmoles/min	-.11	.02	.40	- .29	-.05	-.05
Calcium, mmoles/min	1.40	-.83	6.13	.04	2.96	3.26
Sulfate, mmoles/min	.31	.44	.14	.30	.50	.53
Magnesium, mmoles/min	.03	-.02	-.01	- .01	-.12	-.12
Chloride, mmoles/min	.01	.01	0	- .02	0	0
Nitrate, mmoles/min	.03	0	0	.01	0	0
Carbonate, mmoles/min	0	.01	-.98	-2.69	-.01	-.01

the mix tank did not allow any magnesium to remain in solution. Chloride, nitrate and sodium were not leached to any significant degree in these experiments. In both the first and the third experiments, no significant change in the total carbonate level was measured. In the second experiment, a substantial amount of carbonate dropped out of solution in the tank. Even though calcium carbonate was dropping out of solution in all three experiments, the total amount of carbonate species was much larger in the second experiment. The carbonate level in the tank was higher in Experiment 2 because CO_2 was bubbled into the pond and the pond water was recycled into the tank. In Experiment 1, CO_2 was not bubbled into the pond and in Experiment 3 the pond water was not recycled.

Using Equation 3-2, the weight percent of each species leached from the ash was calculated.

$$W = \frac{D \cdot MW}{F} \times 100 \qquad (3\text{-}2)$$

The results of these calculations are presented in Table 3-7.

TABLE 3-7. COLSTRIP FLY ASH REACTIVITY

	Experiment 1	Experiment 2	Experiment 3
Calcium, wt. %	0.08	0.82	0.83
Sulfate, wt. %	0.24	0.14	0.33
Magnesium, wt. %	0.0	0.0	0.0

In the first experiment the calcium concentration remained very high because calcium carbonate precipitation was controlled by the low carbonate concentration in the tank and the pond (.08-.04 mmoles/ℓ). The high calcium concentration inhibited the degree to which calcium was leached from the ash. The amount of calcium leached in the second experiment was much greater because the calcium concentration in the leachate was lower due to the supply of carbonate ion in the pond allowing greater precipitation of calcium as $CaCO_3$. In Experiment 3, the calcium concentration was low due to the fact that there was no recycle from the pond.

The sulfate concentration did not vary to the same degree that calcium did. The total amount of sulfate that was leached from the ash in this experiment was less than that which was leached from the ash with deionized water. From other experiments (see Appendix K) performed at pH's 4-8 with deionized water, the weight percent of leachable sulfate ranged from .55 to .60 which is about twice as much as the values presented in Table 3-7.

3.2.3 Conclusions

The results of the three experiments performed with the MPC ash lead to the following conclusions:

1) This ash is very alkaline and therefore causes $CaCO_3$ and $Mg(OH)_2$ scale problems that would not be seen with a less alkaline or an acidic ash.

2) Increased CO_2 transfer in the pond causes the pH to drop in the pond and the tank with recycle, and increase the amount of calcium leached from the ash.

3) The reactivity of this ash decreases with decreasing water quality.

APPENDIX E

COMPUTER MODELS

1.0 INTRODUCTION

In all five power plant studies computer models of the large water consumers at the plants were used to simulate existing and alternative modes of operation. These models were used to predict temperatures, flow rates, and compositions of the important streams in the cooling tower, ash sluicing and SO_2 scrubbing situations found at these power plants.

The purpose of this appendix is to discuss these models in greater detail than is presented in the individual plant studies (Appendices F-J). In Section 2.0 flowsheets and descriptions of the individual models used in this study are presented. Section 3.0 presents descriptions of the individual subroutines used in these models and Section 4.0 describes the basis of the chemical equilibrium program used to predict the compositions of the liquid streams in the models.

2.0 MODEL DESCRIPTIONS

The process simulation used in this study is a group of computer programs for simulating aqueous inorganic chemical processes. The programs include an executive system and a set of equipment subroutines. The function of the executive system is to interconnect the various units in the appropriate fashion and control the sequencing of the computer operations.

The process units are interconnected by means of a process matrix during an initialization phase of computer operations. In this phase, model input data are read into the machine, the process matrix is used to define the processing scheme, and each equipment box is initialized. Each processing unit is labeled by a number called an equipment number and the subroutine designation. Each process stream is labeled by a stream number.

The process matrix used to define each processing scheme is given on the first page of computer printout for each simulation case. Each process unit is listed in the process matrix. Input and output stream vectors are assigned to each unit so that the interconnections specified in the process matrix correspond to the interconnections of the process flow diagram.

The executive system also must be given the order in which the process calculations are to be made. This order is indicated immediately under the process matrix in the printout. To execute the process calculations, the executive system takes each subsequent equipment number from the order of calculations and determines the subroutine name and the input and output streams from the process matrix.

In this section descriptions of the models used to simulate the ash sluicing, cooling tower and SO_2 scrubbing systems are presented. This includes flowsheets of the models, an explanation of what each subroutine represents in the flowsheet and descriptions of the actions required of the executive system.

In many cases the same model was used to simulate similar systems at different plants. In those cases only one description is presented since the simulations only differed in the inputs to the system and not the structure of the system. The headings for each subroutine include the names of the plants where these models were employed.

2.1 Ash Sluicing (Bowen, Montour, Comanche)

Two of the power plants studied (Bowen and Montour) employed wet ash sluicing to dispose of the ash produced from the combustion of the coal. One of the plants (Comanche) sluiced bottom ash but used dry methods to dispose of the fly ash collected in the electrostatic precipitator. The model used to simulate the ash sluicing operations at these three plants is discussed in this section.

Figure 2-1 presents the flow sheet of the ash sluicing simulation used to simulate the ash sluicing operations at Bowen, Montour, and Comanche. This flowsheet identifies the input subroutines, used to calculate the initial streams, the equipment subroutines, used to model individual pieces of equipment, the overall system balance subroutine, and the order of calculations. The input subroutines are shown as circles, the equipment subroutines are represented by rectangles, and the overall system balance is placed in the upper-right hand corner. Descriptions of the individual subroutines are presented in Section 3.0.

The order of process calculations is presented at the bottom of Figure 2-1. The numbers are presented in the order in which the corresponding subroutines are called by the executive system. The order of calculations indicates that the inputs are initialized by calling the input subroutines. Then the equipment and system balance subroutines are called. These subroutines specify the composition of all the streams numbered in Figure 2-1.

Several assumptions were made in modeling ash sluicing systems with this simulation. These include:

1) Ionic reactions taking place in the liquid phase are rapid and thus at equilibrium.

2) Solid-liquid equilibrium is achieved in the ash pond, with the exception of $CaSO_4$ which is allowed to remain supersaturated.

3) Ash dissolution is essentially complete before the slurry reaches the pond.

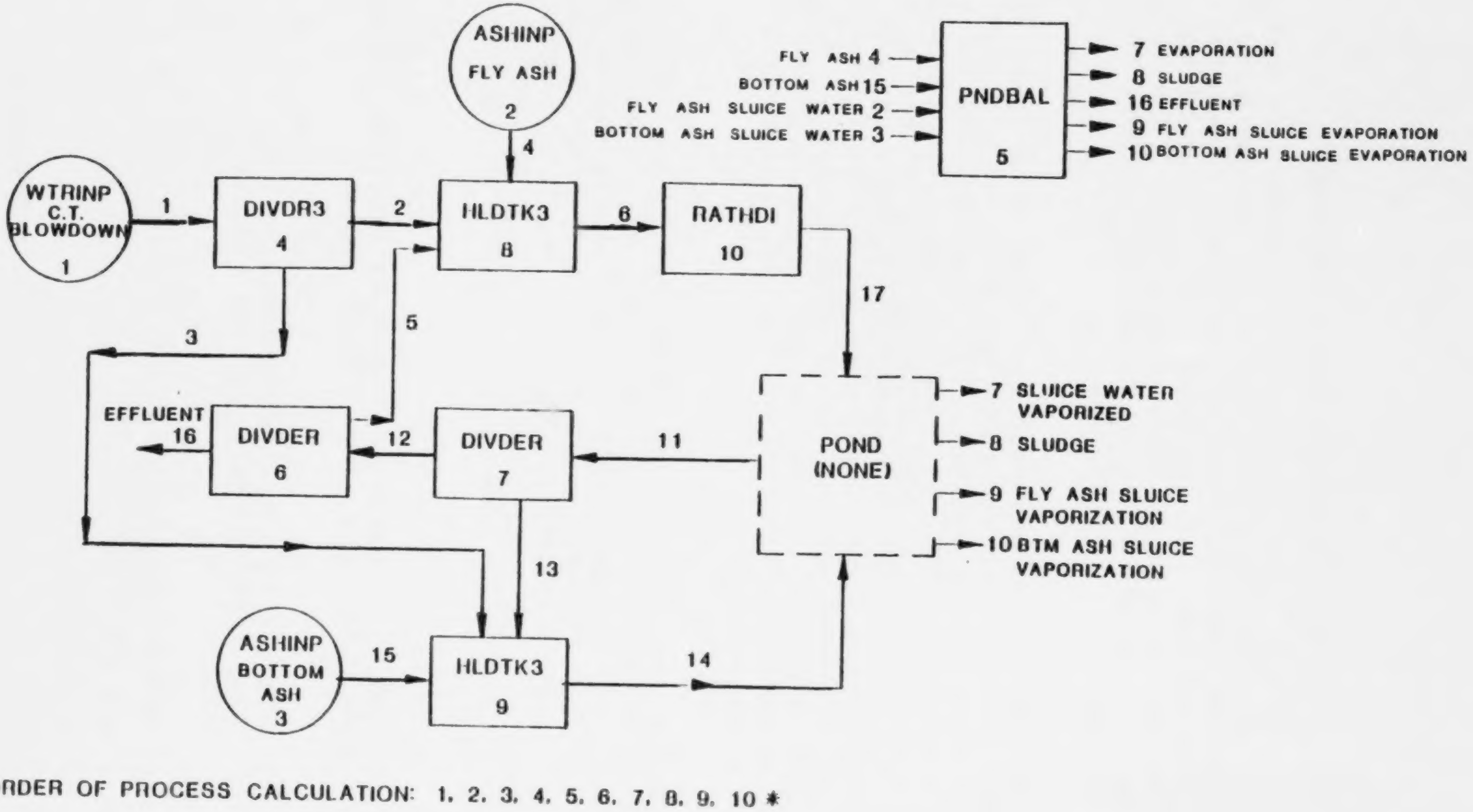

Figure 2-1. Ash sluicing simulation flow scheme.

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4) All solids precipitation occurs in reaction vessels or the pond. RATHD1 calculates nucleation amounts and then precipitation rates based on kinetic expressions.

5) Subroutine RATHD1 models nucleation as an instanteous rate if the species' relative saturation exceeds the critical value. Nucleation is allowed such that the various species' relative saturations are returned to their respective critical levels. At this point, no further nucleation is allowed.

2.2 Cooling Tower Model

Four of the power plants studied employed cooling towers to dispose of waste heat from the condensers. Three of the plants (Bowen, Montour and Colstrip) employed cooling systems with hot side blowdown. The other plant (Comanche) took its blowdown before the condenser and therefore had a much cooler blowdown stream. The models of these two types of cooling systems differed slightly and will be discussed separately.

2.2.1 Hot Side Blowdown at Bowen, Montour and Colstrip

Figure 2-2 presents the flow sheet of the cooling tower simulation used to simulate the cooling systems at Bowen, Montour and Colstrip. This flow sheet identifies the input subroutines, used to calculate the initial streams, the equipment subroutines, used to model the individual pieces of equipment, the overall system balance subroutine, and the order of calculations. The input subroutines are shown as circles, the equipment subroutines are represented by rectangles, and the overall system balance is placed in the lower-right hand corner. Descriptions of the individual subroutines are presented in Section 3.0.

The order of process calculations is presented in the lower-left hand corner. The numbers are presented in the order in which the corresponding subroutines are called by the executive system. The order of calculations in Figure 2-1 indicates that the inputs are initialized and the first approximation of the cooling tower inlet water is calculated by CTGES. CLGTR1 then computes the outlet air rate and composition, the amount of water evaporated, and the outlet water and drift compositions.

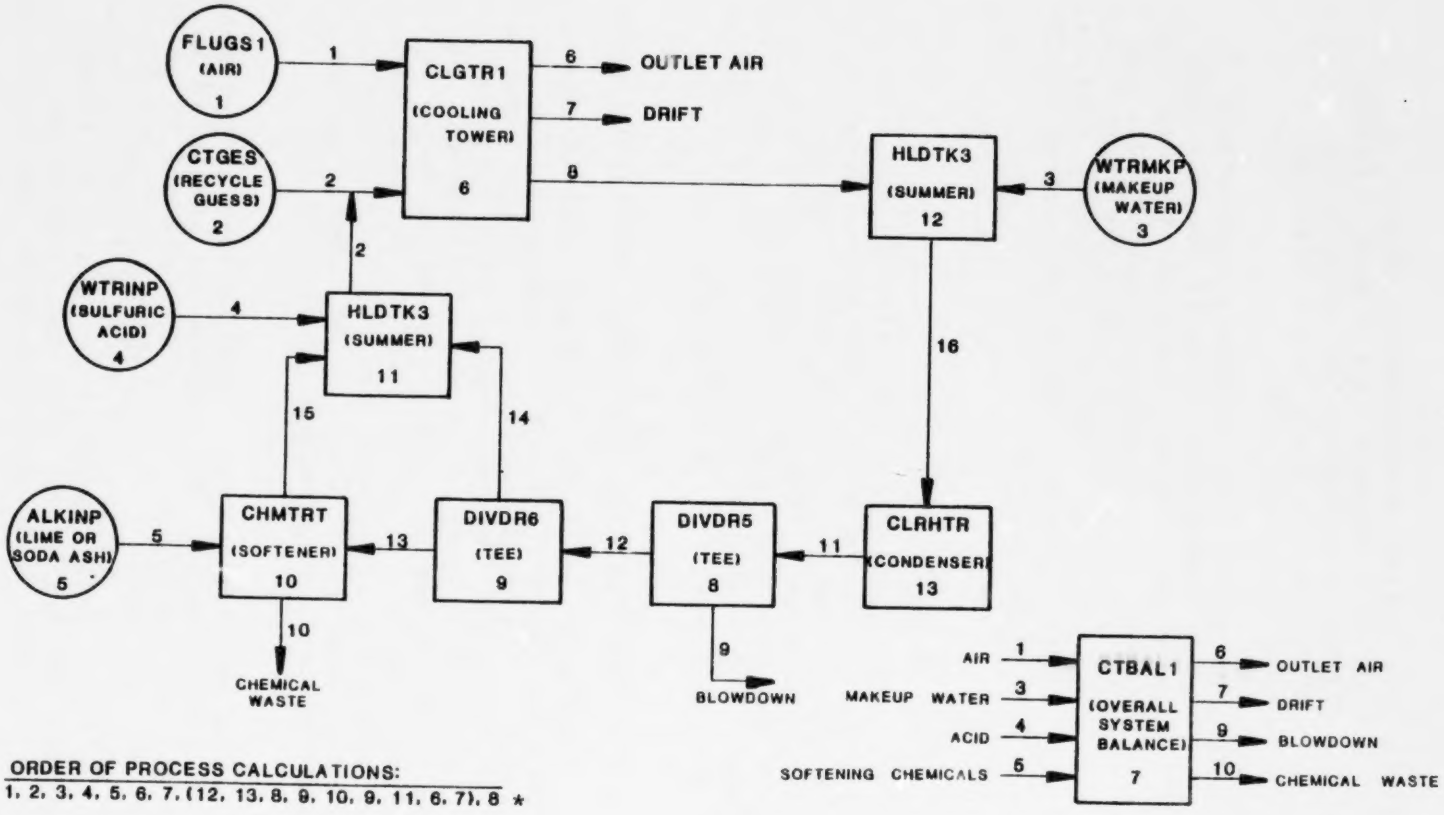


Figure 2-2. Hot side blowdown cooling tower simulation flow scheme.

Next, CTBAL1 computes the blowdown composition and flow. The convergence loop is entered through DIVDR5 which calculates the circulating water composition. Calculations are performed around the loop to CLGTR1 which calculates a new air rate and drift composition. CTBAL1 then calculates a new blowdown stream.

At this point, the species concentrations of the blowdown stream are compared to the previous values. If the differences in concentration of each species for consecutive iterations are within the specified convergence criteria, the convergence scheme is completed. If not, the cycle is repeated.

This model calculates the temperature, flows and compositions of all the streams which are numbered in Figure 2-2. This model determines the amount of acid, if any, necessary to control $CaCO_3$ scale. This model further determines if softening is required to control $CaSO_4 \cdot 2H_2O$ scale and how much lime is necessary.

This model has four major assumptions associated with it. These include:

1) Equilibrium exists with respect to CO_2 and H_2O in the atmosphere and cooling tower exit water.

2) Ionic reactions taking place in the liquid phase are rapid and thus at equilibrium.

3) The temperature of the cooled water stream approaches the wet bulb temperature of ambient air within a predictable range.

4) The compositions and temperatures of the cooled water and drift streams are equal.

The assumption involving the temperature of the cooled water stream is a recognized design parameter in cooling tower evaluation and gives a good approximation. The assumption concerning the temperature and composition of the drift stream should be very close to actuality as is the assumption in regard to H_2O gas-liquid equilibrium. The assumption with regard to

CO_2 equilibrium is conservative since the partial pressure of CO_2 in actual cooling towers tends to be greater than the equilibrium value. The lower equilibrium concentration of carbonate species, assumed in the model, causes the pH to be slightly higher in the model than in actual operation. The higher pH causes the relative saturation of $CaCO_3$ to increase more than the lowered carbonate species concentration causes it to decrease.

2.2.2 Cold Side Blowdown at Comanche

Figure 2-3 presents the flowsheet of the cooling tower simulation used to simulate the cooling system at Comanche. This flowsheet identifies the input subroutines, used to calculate the initial stream, the equipment subroutines, used to model the individual pieces of equipment, the overall system balance subroutine and the order of calculations. The input subroutines are shown as circles, the equipment subroutines are represented by rectangles, and the overall system balance is placed in the lower-right hand corner. Descriptions of the individual subroutines are presented in Section 3.0.

The order of process calculations is presented in the lower left hand corner of Figure 2-3. The numbers are presented in the order in which the corresponding subroutines are called by the executive system. The order presented in Figure 2-3 indicates that the inputs are initialized and the first approximation of the cooling tower inlet water is input by WTRINP. CLGTR1 then computes the outlet air rate and composition, the amount of water evaporated, and the outlet water and drift composition. Next CTBAL1 computes the blowdown composition and flow. The convergence loop is entered through DIVDR5 which calculates the circulating water composition. Calculations are performed around the loop to CLGTR1 which calculates a new air rate and drift composition. CTBAL1 then calculates a new blowdown stream.

At this point, the species concentrations of the blowdown stream are compared to the previous values. If the differences in concentration of each species for consecutive iterations are within the specified convergence criteria, the convergence scheme is completed. If not, the cycle is repeated.

This model calculates the temperatures, flows and compositions of all the streams which are numbered in Figure 2-3. This model determines the amount of acid, if any, necessary to control $CaCO_3$ scale. This model further determines if softening is required to control $CaSO_4 \cdot 2H_2O$ scale and how much lime is necessary.

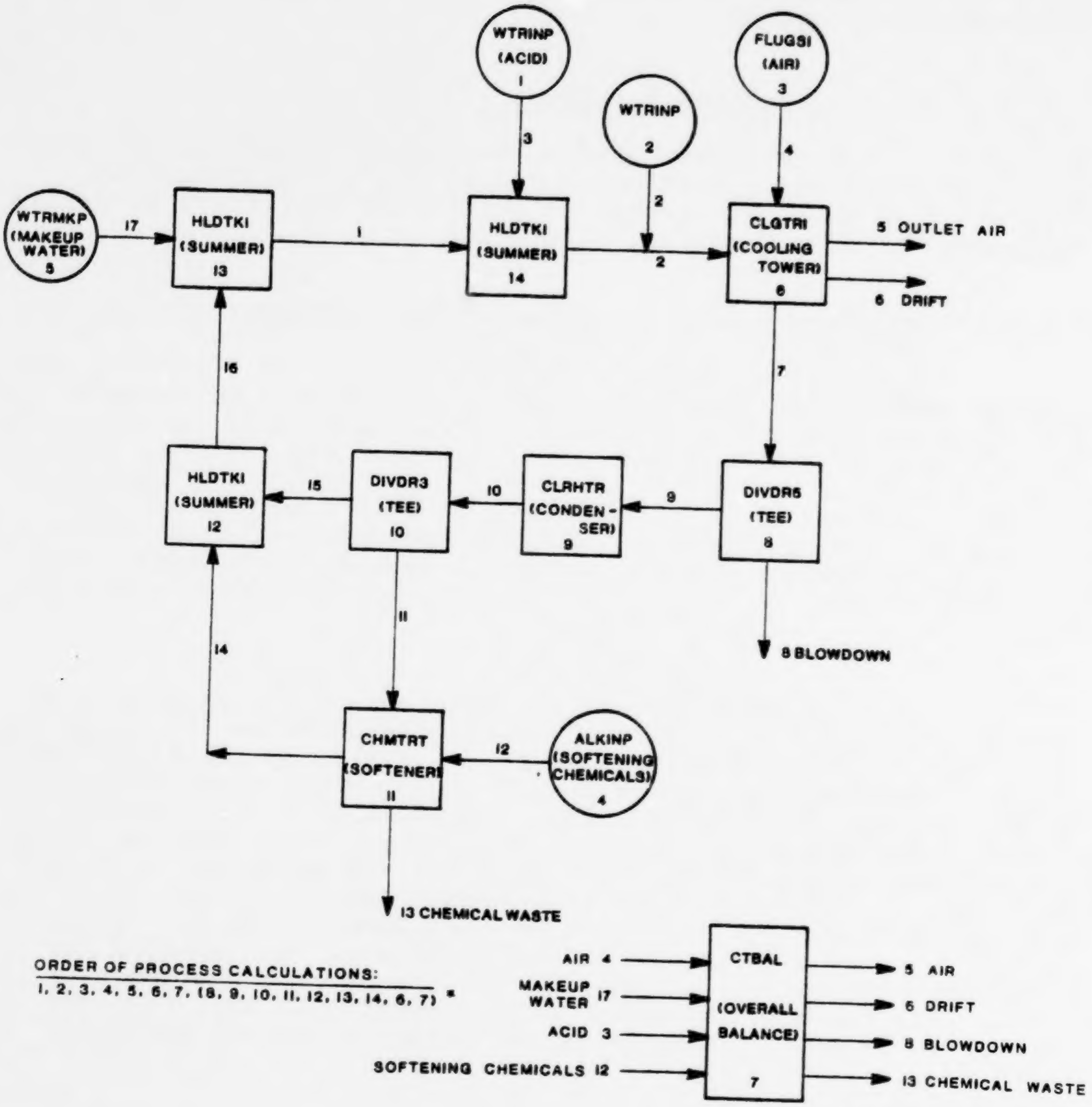


Figure 2-3. Process simulation scheme for Comanche cooling tower system.

The assumptions associated with this model are identical to those presented in Section 2.2.1 for the cooling tower model with hot side blowdown.

2.3 SO_2-Particulate Scrubbing

Two of the power plants studied (Four Corners and Colstrip) employed wet scrubbing to remove SO_2 and particulates from the flue gas. The design of the systems differ to a certain degree and will be discussed separately.

2.3.1 SO_2-Particulate Scrubbing at Four Corners

Figure 2-4 presents the flowsheet of the scrubbing simulation used to simulate the scrubbing system at Four Corners. The flowsheet identifies the input subroutines, used to calculate initial streams, the equipment subroutines, used to model individual pieces of equipment, the overall system balance subroutine and the order of calculations. The input subroutines are shown as circles, the equipment subroutines are represented as rectangles and the overall system balance is placed to the side. Descriptions of the individual subroutines are presented in Section 3.0.

The order of process calculations is presented at the bottom of Figure 2-4. The numbers are presented in the order in which the corresponding subroutines are called by the executive system. Once the inputs are initialized and the first approximation for the thickener overflow (Stream 15) is made, SYSTB4 computes the compositions and flow rates for stack gas and scrubber effluent streams. Then calculations are performed in Boxes 8, 9, and 10. At this point, the composition of Stream 15 is compared with the previously calculated composition for this stream. If the differences in composition of each species for consecutive iterations are within the specified convergence criteria, this convergence scheme is completed. If not, then new values for Stream 15 components are assigned and the cycle is repeated.

Once this convergence is finished, the remainder of the stream computations are performed. First, the scrubber calculations (Equipment Boxes 11 and 12) are made. Next, the thickener underflow composition is determined in Equipment Box 13, and the sluicing operation simulated in Equipment Box 14. The composition of the scrubber recycle loop makeup (Stream 19) is computed in Equipment Box 15. Finally, the fan and reheat requirements are computed in Boxes 16 and 17.

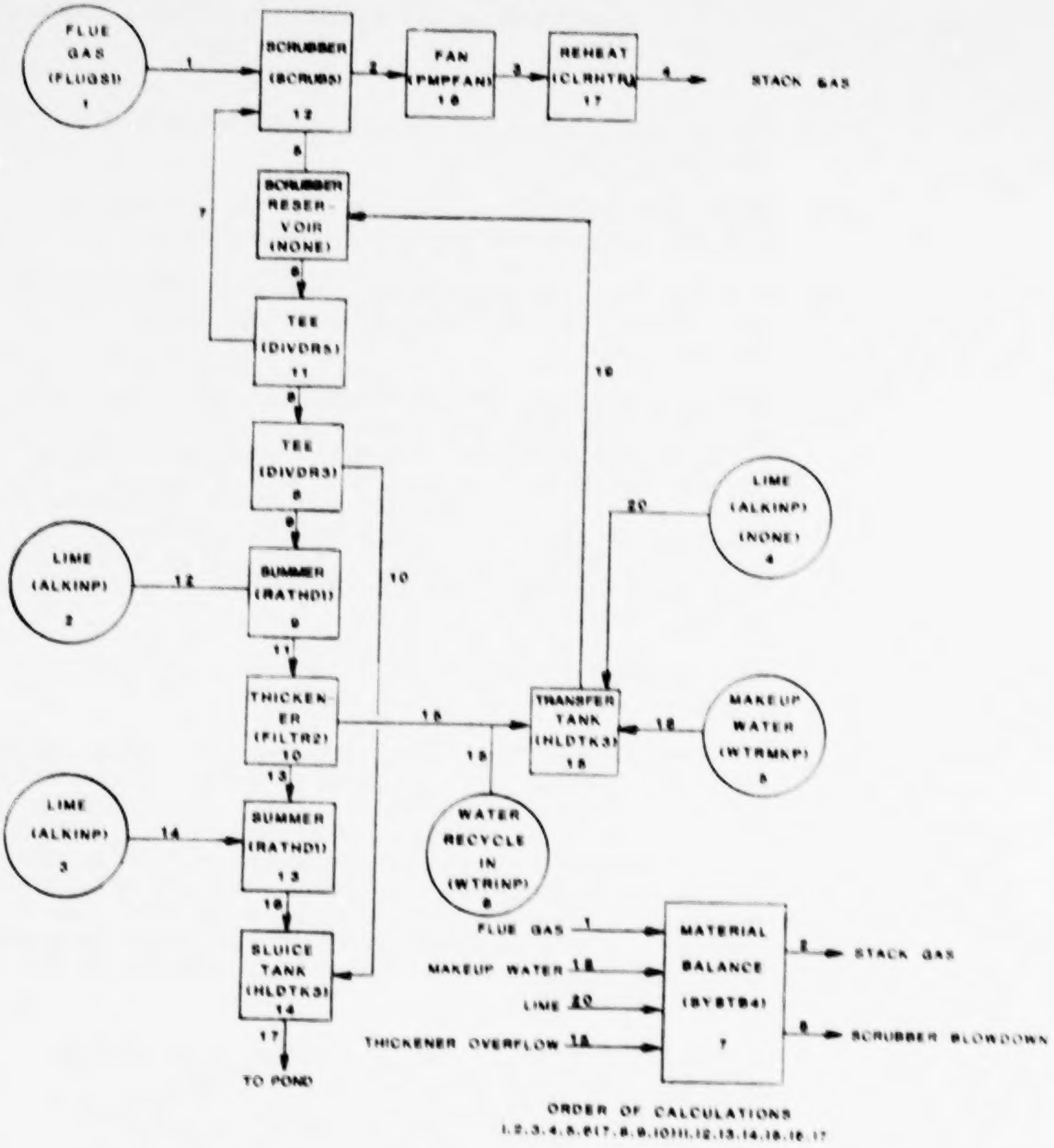


Figure 2-4. Four Corners scrubbing simulation scheme (existing operations).

Several assumptions are inherent in performing this simulation with the subroutines outlined above. These assumptions are enumerated below:

1) The stack gas is saturated with respect to H_2O.

2) Equilibrium exists between CO_2 in the stack gas and liquor in the scrubber bottoms.

3) The scrubber bottoms and stack gas temperatures are the adiabatic saturation temperature of the flue gas.

4) The scrubber was modeled without allowing solids precipitation to occur. However, dissolution of $Mg(OH)_2$, $Ca(OH)_2$, and $CaSO_3 \cdot \frac{1}{2}H_2O$ solids entering the scrubber was allowed. This dissolution pertains to particulates removed as well as slurry solids entering the scrubber. The fraction of each solid species that will dissolve in the scrubber is specified by the user.

5) All oxidation was assumed to occur in the scrubber.

6) In Subroutine SYSTB4, no $CaSO_4 \cdot 2H_2O$, $CaSO_3 \cdot \frac{1}{2}H_2O$, or $CaCO_3$ solids are allowed to form. This was done to model the scrubber blowdown stream as accurately as possible. Realistically, actual conditions are somewhere between no precipitation and solid-liquid equilibrium. The short residence time in the scrubbing loop and the low inventory of precipitating solid crystals indicate that the assumption of no solids formation in the loop is adequate.

7) All solids precipitation occurs in reaction vessels (Subroutines HLDTK3 or RATHD1). HLDTK3 assumes solid-liquid equilibrium is achieved. RATHD1 calculates nucleation amounts and then precipitation rates based on kinetic expressions.

8) Subroutine RATHD1 models nucleation as an instantaneous rate if the species' relative saturation exceeds the critical value. Nucleation is allowed such that the various species' relative saturations are returned to their respective critical levels. At this point, no further nucleation is allowed.

9) Ionic reactions taking place in the liquid phase are rapid and thus in equilibrium.

A different model was used to simulate the alternatives at Four Corners. In Figure 2-5 a flowsheet of the model used for Alternative 3 is presented. A description of this model only is presented because it is the most complicated alternative model and contains most of the features of the other models.

The order of process calculations is somewhat altered in this simulation compared to the preceding one. The three input routines, FLUGS1, ALKINP, and WTRMKP, again initiate the computations. At this point, Subroutine WTRINP provides an initial estimate of the flow rate and composition of the ash pond overflow stream (Stream Number 13).

Next is the beginning of the first convergence routine. Subroutine SYSTB4 performs overall material and energy balances in computing the FILTER underflow stream (Stream Number 5). Then, EVAPND and FILTR2 are used to model the ash pond. These three routines (SYSTB4, EVAPND, and FILTR2) are repeated until the compositions in Stream Number 13 are consistent for consecutive iterations. After the second iteration, a convergence scheme is implemented to facilitate this convergence.

Once the ash pond overflow stream flow rate and composition have been determined, the overall material balances are correct. Then the next convergence loop is entered. Computations are repeated in the slurry recycle loop (Subroutines SCRUB5, RATHD1, and DIVDR2) until the scrubber feed stream composition has converged.

The assumptions inherent in the use of this model are identical to those presented for the existing operations model used for the Four Corners system.

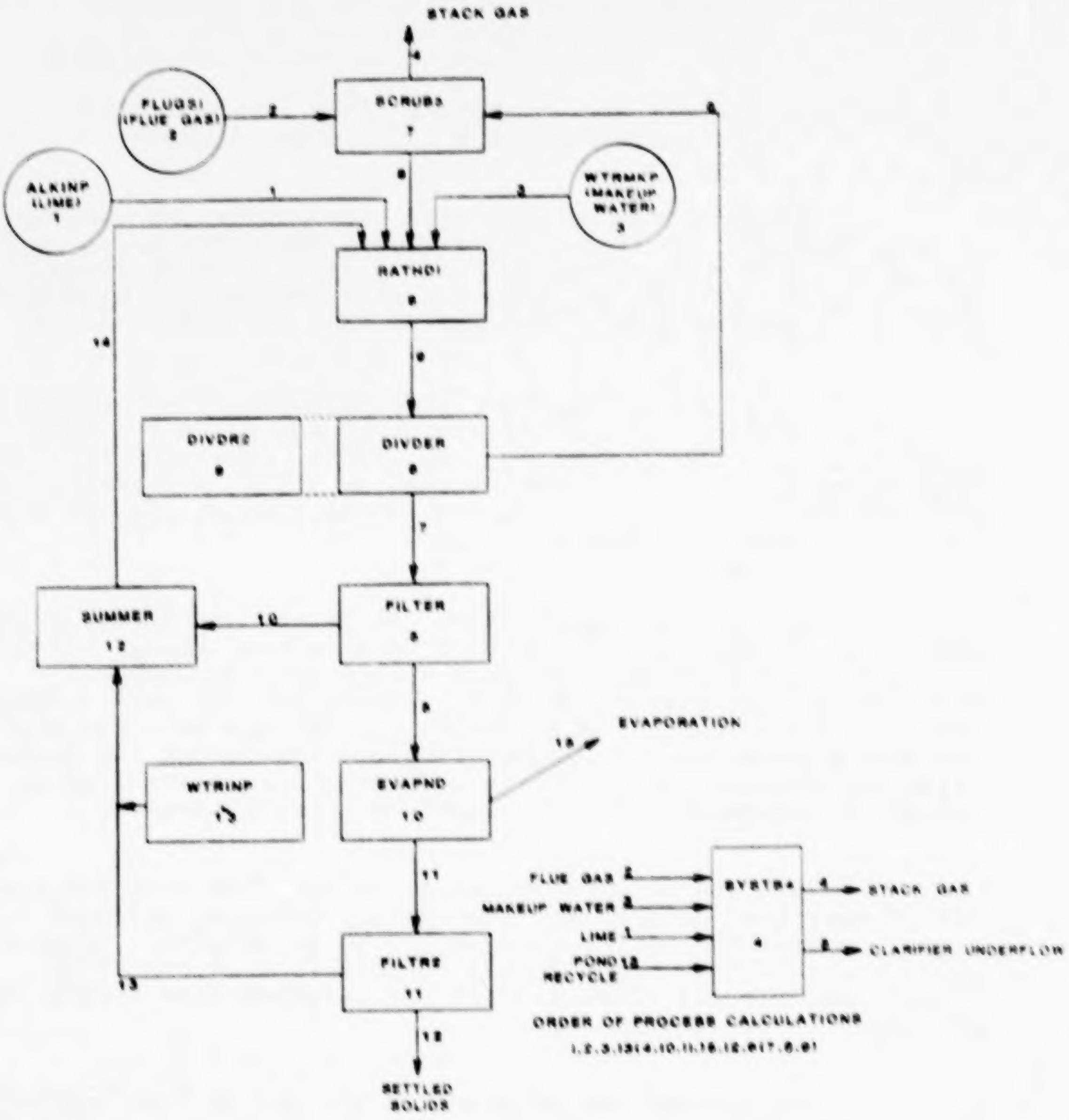


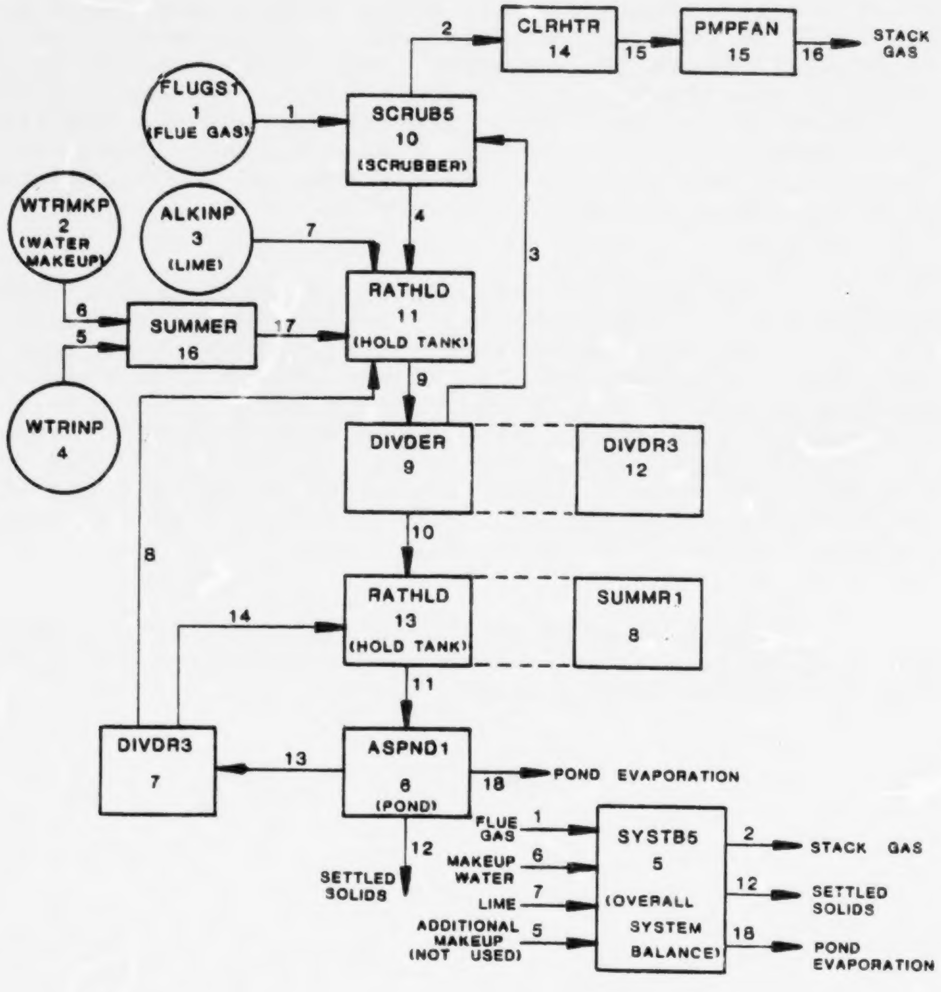
Figure 2-5. Process model for Four Corners Alternative Three.

2.3.2 SO_2 - Particulate Scrubbing at Colstrip

Figure 2-6 presents the flowsheet of the scrubbing simulation used to simulate the scrubbing system at Colstrip. The flowsheet identifies the input subroutines, used to calculate initial streams, the equipment subroutines, used to model individual pieces of equipment, the overall system balance subroutine, and the order of calculations. The input subroutines are shown as circles, the equipment subroutines are represented by rectangles and the overall system balance is placed in the lower right hand corner. Descriptions of the individual subroutines are presented in Section 3.0.

The order of calculations is presented at the bottom of Figure 2-6. The numbers are presented in the order in which the corresponding subroutines are called by the executive system. The order indicates that the inputs are initialized and overall balance calculations are performed first. Then, iterative calculations are performed around the scrubbing loop (Boxes 10, 11, and 12) until calculated rates are satisfied for the input recycle tank volume. Once this convergence is achieved, calculations around the effluent tank are performed and reheat and fan requirements are calculated.

The assumptions inherent in using this model are identical to those listed in Section 2.3.1 for the simulation of the Four Corners scrubbing model.



ORDER OF PROCESS CALCULATIONS:

1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 5, 6, 7, 8, 9, 16, (10, 11, 12,) 13, 14, 15 *

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Figure 2-6. Colstrip scrubbing simulation flow scheme.

3.0 SUBROUTINE DESCRIPTIONS

In this section descriptions of all the subroutines used to model the water systems in this study are presented. These include three separate classes which will be described separately. Section 3.1 is devoted to input subroutines, Section 3.2 discusses the equipment subroutines, and the system balance subroutines are covered in Section 3.3.

3.1 Input Subroutines

The ALKINP subroutine enters any of the following species into the simulation system: CaO, MgO, $CaCO_3$, $MgCO_3$, $CaSO_3$, $MgSO_3$, $CaSO_4$, $MgSO_4$, $Ca(OH)_2$, $Mg(OH)_2$, and inerts. ALKINP is used in conjunction with a hold tank or chemical treatment routine to add a solid stream of these compounds to the simulation flow scheme. In order to specify this solid stream, ALKINP requires the total flow rate and the weight fractions of the solid species. ALKINP was used in the cooling tower models as a source of chemicals to the system in cases where softening was required to prevent $CaSO_4 \cdot 2H_2O$ scale. It was also used in the scrubbing model for the Four Corners plant as a source of alkali additive.

The subroutine ASHINP originates a solid ash stream with specified flow rate and composition. Composition is input as soluble weight fractions of CaO, $CaSO_4$, MgO, $MgSO_4$, $MgCl_2$, Na_2O, and NaCl. The insolubles in the ash are all input as inerts. In the ash sluicing simulations, ASHINP is used to originate both the bottom ash and fly ash inputs.

The CTGES subroutine is a subroutine, used only in cooling tower simulations, which generates an initial guess of the composition and temperature of the process water entering the cooling tower. This is done by multiplying the concentration of the ionic species in the makeup water by the cycles of concentration, except for $CO_3^=$ and $SO_4^=$. The $CO_3^=$ is specified as that which is in equilibrium with the atmosphere. The $SO_4^=$ is the value necessary to attain an input pH, thereby allowing the subroutine to take acid addition into account.

The FLUGS1 subroutine is a general flue gas stream simulation routine. It provides an input stream based on specified values of gas properties and fly ash properties. The gas properties are temperature, pressure, flow rate, and mole fraction composition. Fly ash properties include flow rate and weight fraction composition with respect to CaO, $CaSO_4$, MgO, Na_2O, NaCl, and inerts. FLUGS1 was used in all of the scrubbing models studied. This subroutine was also used in the cooling tower models to initiate the inlet air stream. No fly ash was included in the cooling tower simulations.

There are two water input subroutines, WTRMKP and WTRINP. The concentration of the major ionic components which normally occur in water are specified by both routines. The ions in solution may include $SO_3^=$, $SO_4^=$, $CO_3^=$, NO_3^-, Cl^-, Ca^{++}, Mg^{++}, and Na^+. The difference is that the liquid flow rate of the output stream from WTRINP is input by the user, whereas the flow rate associated with the WTRMKP output stream is computed by the material balance within the simulation. WTRINP is used in all of the models used in this study. It was used to specify the makeup water in the ash sluicing model, the acid stream in the cooling tower model, and to estimate the recycle streams in the scrubbing models. WTRMKP is only used in the cooling tower and scrubbing models. In both cases it is used to specify the composition of the makeup water to the system.

3.2 Equipment Subroutines

The pond system at Colstrip was modeled by ASPND1. The solid waste weight fraction solids and the pond evaporation rate are specified as inputs to this subroutine. This subroutine calculates the composition of the recycle from the ash pond.

The CHMTRT subroutine is used only in the cooling tower models. This subroutine is used in conjunction with CTBAL1 to remove Ca^{++} from the cooling cycle by means of chemical treatment. The subroutine simulates the operation of a number of treatment options which can remove either Ca^{++}, or Mg^{++} and Ca^{++}. CHMTRT is set up to model side-stream treatment of the recirculating cooling water and requires an initial guess of how much water is diverted for treatment. Using the input of the required calcium removal rate determined in CTBAL1, this initial treatment water flow rate is adjusted to give the desired calcium removal rate for the specified treatment option. The treatment options include the following:

1) Lime treatment for Ca^{++} and Mg^{++} removal.
2) Lime treatment for Ca^{++} removal.

3) Lime-soda ash treatment for Ca^{++} and Mg^{++} removal.

4) Lime-soda ash treatment for Ca^{++} removal.

5) Caustic soda treatment for Ca^{++} and Mg^{++} removal.

6) Caustic soda treatment for Ca^{++} removal.

7) Sodium zeolite treatment for Ca^{++} and Mg^{++} removal.

Stoichiometric factors for chemical addition must be specified. The weight fraction solids in the chemical addition stream and the waste stream must also be specified.

Output information from CHMTRT includes the rate and composition of the chemical addition stream, the adjusted flow rate for entering water, the composition and flow rate for treated water, and the composition and flow rate of the waste stream.

The CLGTR1 subroutine simulates the operation of a wet cooling tower. The following data are required as input information for this routine: complete specification of ambient air, specification of drift rate, complete specification of cooling water entering the cooling tower, specification of ambient wet bulb temperature, specification of the temperature approach of the cooling water leaving the cooling tower to the ambient wet bulb temperature, and specification of the relative saturation of the exit air with respect to water. CLGTR1 uses this information in heat and material balance calculations to determine the amount of water evaporated. Knowing this in turn allows the cooling tower exit air to be completely determined. The composition of the water stream leaving the cooling tower, which is also assumed to be the composition of the drift, is then found.

The CLRHTR subroutine serves the function of a heat exchanger in the cooling tower and scrubbing models. It changes the temperature of liquid and gaseous streams and performs enthalpy calculations to determine the heat duty. In the cooling tower models CLRHTR is used to simulate the condenser. In the scrubbing models it is used to simulate the reheat required to send the flue gas up the stack.

Four subroutines DIVDER, DIVDR3, DIVDR5, and DIVDR6 simulate process "tees" and are used to split streams. DIVDER requires complete information about one effluent stream and the flow of the other effluent stream to calculate the flow rate and composition of the feed stream. DIVDR3 calculates the flow and composition of one effluent stream from complete information about the feed stream and the flow of the other effluent stream. DIVDR5 requires complete information about one effluent stream and the flow rate for the feed stream in order to entirely specify the feed stream and the second effluent stream. DIVDR6 requires the input of a completely specified feed stream along with the flow rate of the first effluent stream in order to completely specify both effluent streams.

Subroutine EVAPND models an evaporation pond. Based on the area of the pond and certain climatological data, this routine will compute the evaporation rate and the equilibrium composition of the material remaining in the pond. EVAPND is used in the scrubbing models.

Subroutine FILTER models a solid-liquid separator (i.e., a clarifier or vacuum filter). The filter bottoms stream must be completely specified and the filtration efficiency must be provided. With these inputs FILTER computes the flow rate and compositions of both the filter feed and the filter overflow streams. An assumption that complete solid-liquid equilibrium is reached in the separation device is made when Subroutine FILTER is used. FILTER is used in the scrubbing models.

The HLDTK3 subroutine simulates an equilibrium reaction vessel. All of the input streams must be specified with respect to composition and flow rate. HLDTK3 will then use this information to generate an output stream. Mass balances and the equilibrium program are used to calculate an output stream with species in solid-liquid equilibrium. HLDTK3 is used in the cooling tower and ash sluicing models.

PMPFAN is a subroutine which calculates the fan requirements to blow the stack gas up the stack. This subroutine is used in the scrubber models.

RATHLD was used in the scrubbing model at the Colstrip Plant. Process tanks in the system were modeled by RATHLD. Both the scrubber recycle tank and the effluent tank where the scrubber blowdown is diluted from 12% to 6% solids were included. Solid precipitation rates were calculated based on the tank volume, slurry flow rate, and precipitation kinetics data for $CaSO_3 \cdot \frac{1}{2}H_2O$ and $CaSO_4 \cdot 2H_2O$. Detailed documentation of the subroutine RATHD1 is presented at the end of this section. RATHD1 was used to model reaction vessels and was developed specifically for this study.

The SCRUB5 subroutine is used to model a concurrent contactor. SCRUB5 is used in the scrubbing models to simulate the venturi scrubber. It performs the appropriate vapor-liquid mass transfer calculations based on specific SO_2, CO_2, and particulate sorption efficiencies and H_2O vaporization rate. The scrubber gas and slurry effluent streams are computed, by this subroutine.

The subroutine SUMMER simply sums the input streams to calculate an output stream. Flow rates of all species are computed in this routine. SUMMR1 calculates one of the input streams using complete composition and flow information about the other input and output streams. Both of these subroutines are used in the scrubber simulations.

RATHD1: Rate Hold Tank 1

Function:

This routine simulates a process hold tank with up to four input streams. Complete information about the input streams and hold tank volume must be provided. A surface area-dependent solid-liquid mass transfer rate determination is employed and $CaSO_3 \cdot \frac{1}{2}H_2O$, $CaSO_4 \cdot 2H_2O$, and $CaCO_3$ solid precipitation rates are calculated.

Input Information:

Input stream compositions and flow rates as well as the tank volume must be supplied. The inlet crystal sizes for $CaCO_3$, $CaSO_3 \cdot \frac{1}{2}H_2O$, and $CaSO_4 \cdot 2H_2O$ may also be specified. If these areas are not specified they will be calculated.

Output Information:

The output stream will be completely specified. The average solid crystal area and the nucleation and precipitation rates for the appropriate species are also computed.

Description:

First, the input parameters are converted from input units to program units.

The next step in these calculations is to determine the molar rates of the key species in the effluent stream ($n_{OS,jt}$, jt = all key species, gmole/sec). This calculation is performed by subroutine ADDER, which adds the molar rates of the key species in the input streams ($n_{S,jt}$, for S = I_1 through I_4).

$$n_{OS,jt} = \sum_{S = I_1}^{I_4} n_{S,jt} \qquad (1)$$

for jt = all key species. Subroutine ADDER also determines the solids flow rates into the rate hold tank.

$$n_{I,js} = \sum_{S = I_1}^{I = I_4} n_{S,js} \qquad (2)$$

for js = $CaSO_3 \cdot \frac{1}{2}H_2O$, $CaSO_4 \cdot 2H_2O$, and $CaCO_3$.

ADDER also calculates an average inlet particle size for each of the precipitating species. (This calculation is based on a mass average). If the inlet crystal area is zero, an area of 7500 cm^2/gram is set. If an inlet crystal area is specified in RATHD1 this value overrides the calculated value.

The subroutine next calculates the nucleation rates. First, to determine which species may nucleate, subroutine EQUILB is called allowing supersaturation. Evaluation of the relative saturations of $CaCO_3$, $CaSO_3 \cdot \frac{1}{2}H_2O$, and $CaSO_4 \cdot 2H_2O$ determines if nucleation will occur. Specifics concerning these evaluations are provided in the subsequent discussion.

The parameter APD (Activity Product Divisor) is set according to the relative saturation results. The Activity Product Divisor is used in the equilibrium program in calculating equilibrium compositions. For example, one of the simultaneous equations that is solved by Subroutine EQUILB is shown in Equation 3.

$$\frac{a_{Ca^{++}} \, a_{SO_4^{=}} \, a^2_{H_2O}}{\text{APD (4)}} \leq K_{SP(CaSO_4 \cdot 2H_2O)}$$

In this equation the a's represent the activities of the various species and $K_{SP(CaSO_4 \cdot 2H_2O)}$ is the solubility product constant for calcium sulfate dihydrate. Similar expressions can be written for each precipitating species. The parameter APD had different values depending on whether a particular species is subsaturated or supersaturated.

The tests performed in checking for nucleation are as follows:

1. If the relative saturation of a species is less than or equal to one, the APD_i parameter is not set in RATHD1 and remains equal to one. This makes that species an equilibrium species.

2. If the species' relative saturation is between one and the critical value for the onset of nucleation, APD_i is specified to be a large number (i.e., 1000 times K_{SP}). This allows the relative saturation of a metastable solid to be unrestricted and no nucleation occurs.

3. If the species' relative saturation exceeds the critical value, APD_i is set equal to the critical relative saturation. This allows the solids to precipitate (nucleate) when subroutine EQUILB is called.

Should conditions for nucleation exist, subroutine EQUILB is employed to compute the rate of nucleation for each nucleating species and the solid and liquid species distribution. (Nucleation is modeled as an instantaneous rate and, as such, is independent of hold tank volume.) At this point, an average surface area per gram of solid is computed by the following equation.

$$SAG_{js} = \frac{(SAPG_{js})(XNN_{js}) + (SAGS_{js})(XNS_{js})}{XNN_{js} + XNS_{js}} \qquad (3)$$

where

js = the nucleating species, ($CaCO_3$, $CaSO_3 \cdot \frac{1}{2}H_2O$ and $CaSO_4 \cdot 2H_2O$)

SAG = surface area per gram of solid after nucleation has occurred

SAPG = surface area per gram of nuclei

SAGS = surface area per gram of solid entering the rate hold tank

XNN = mass of the nuclei

XNS = mass of the solid seed entering the hold tank

Once nucleation has been computed, precipitation of solids from the metastable supersaturated liquor is calculated. The form of the rate expression is shown in Equation 4.

$$R_{js} = k_{js}\ SAG_{js}\ MW_{js}\ m_{OS,js}\ \rho H_2O(1)\ (T_{OS}) \cdot V\ (\Pi a_{js} - K_{SP,js})\ /\ 1000.0 \qquad (4)$$

The quantities used in Equation 4 are defined as follows.

R_{js} = precipitation rate (gmole/sec) of solid js, i.e., $n_{OS,js} - n_{I,js}$.

k_{js} = precipitation rate constant (gmole/sec cm^3) for solid js.

MW_{js} = molecular weight (g/gmole) of solid js.

$m_{OS,js}$ = molality of solid js in the output stream (gmole/kg liq H_2O).

$\rho H_2O(1)\ (T_{OS})$ = density of liquid water (g/cm^3) at the temperature of the output stream (T_{OS}, °K).

V = hold tank volume (cm^3).

$\Pi a,_{js}$ = activity product of the ions which form solid js, for example, $a_{CaSO_4 \cdot 2H_2O} = a_{OS,Ca^{++}} \cdot a_{OS,SO_4^{=}} \cdot (a_{OS,H_2O(1)})^2$.

$K_{SP,js}$ = solubility product constant for solid js.

1000.0 = conversion factor (g/kg).

The parameter VRK (VRK = $k_{js} \cdot V \cdot SAG_{js}/1000$), a volumetric rate constant, is set in Subroutine RATHD1 and rates are calculated in Subroutine RATE. The actual mechanism for determining the precipitation rates is to calculate the total amount of solids leaving the rate hold tank (by solving a set of simultaneous equations) and subtracting the quantity of solid seed crystals which enter the hold tank plus the amount of solids formed by nucleation.

Prior to the calculation of rates, two checks are performed. First, any species which is subsaturated is treated as an equilibrium species. Secondly, if no solid seeds are available for crystallization, no precipitation is allowed (APD_i is set to a high value).

Once precipitation has been calculated, solid crystal area is computed according to Equation 5.

$$SAG_{js} = \frac{(XNN_{js} + PNM_{js})(ANO_{js}) + (XNS_{js} + PSM_{js})(ASO_{js})}{(XNI_{js} + PNM_{js} + PSM_{js})} \quad (5)$$

where

js = solid species

XNN = mass of nuclei

PNM = mass of solid precipitating on the nuclei

XNS = mass of seed

PSM = mass of solid precipitating on the seed crystal

SAG = area of solid exiting the hold tank

ANO = area per gram of the nuclei exiting the hold tank

ASO = area per gram of the seed exiting the hold tank

Subroutine RATHD1 models a well-mixed hold tank. The outlet parameters (compositions, area, etc.) are assumed to be uniform throughout the vessel. Since outlet areas are required to compute the rates, the rate calculations must be repeated until the outlet surface area (for each precipitating species) agrees to within 0.01% for consecutive iterations. When the areas are converged, the calculations in Subroutine RATHD1 are complete.

```
      SUBROUTINE RATHD1(P,$)
      INCLUDE CMMN, LIST
      COMMON                             @COMMON DATA FOR ALL SUBROUTINES
     *SV(30,140),                        @STREAM DATA
     *ISTM(25,10),                       @STREAM CONNECTION ARRAY
     *IDEQP(25),                         @EQUIPMENT NAME
     *ISEQ(30),                          @ORDER OF PROCESS CALCULATIONS
     *PA(25,24),                         @EQUIP,PARAMETERS
     *L(10),                             @FLAGS FOR THE RECYCLE LOOPS
     *NL,                                @CURRENT INDEX
     *LSRL(10),LERL(10),                 @START AND END OF RECYCLE LOOPS
     *WV,XLSU(2),XSO(8),XLD(8),DNAT(9),XA(4),LABEL(13),AH20,XO
      DIMENSION P(24)
      END
      COMMON/PAGE/LINE
      COMMON/SOLIDS/LOCSDS, CKS(10),NHY(10),ESK(10,10),ISK(10),
     *APS(10)
      COMMON/APDRVR/APD(11)
      DIMENSION XNS(11),XNN(11),SAG(11),SAGT(11),Z(11),ANO(11),
     *IFLAG(11)
      DIMENSION RS(2,11),CV(11),VI(11),CLC(11),SAPG(11),PNM(11),
     *XNI(11)
      DIMENSION ZSI(11),PSM(11),ZS(11),ASO(11)
      DATA CV(3)/2.5/CV(5)/3./CV(7)/1.3/
      DATA VI(3)/11.808/VI(5)/20.048/VI(7)/13.793/
      DATA CLC(3)/1.150E-4/CLC(5)/1.591E-4/CLC(7)/1.159E-4/
      DATA SAPG(3)/1.02E5/SAPG(5)/1.26E5/SAPG(7)/1.19E5/
      DIMENSION PP(2), VRK(10)

      LOCSL=ISEQ(NL)
      LIS1=ISTM(LOCSL,1)
      LIS2=ISTM(LOCSL,2)
      LIS3=ISTM(LOCSL,3)
      LIS4=ISTM(LOCSL,4)
      LOS=ISTM(LOCSL,6)
      IF(LIS1.LE.0) LIS1=30
      IF(LIS2.LE.0) LIS2=30
      IF(LIS3.LE.0) LIS3=30
      IF(LIS4.LE.0) LIS4=30
      IF(SV(LOS,2).GT.1.5) RETURN 2
      IF (SV(LOS,2).GT.0.5) GO TO 1
      WNES=0.0
      LINE=LINE + 5
      IF (LINE .LT. 43) GO TO 40
      LINE = 8
      PRINT 98
      CALL DATIME
      PRINT 97,LABEL
      PRINT 96
 40   PRINT 99, ISEQ(NL)
```

```
      GALS=P(1)*7.480519
      PRINT 101, P(1), GALS
      PRINT 102, P(2),P(3),P(4),P(8)
 96   FORMAT(1X, 'SYSTEM AND EQUIPMENT PARAMETERS')
 97   FORMAT(1H+,34X,13A6)
 98   FORMAT(1H1)
 99   FORMAT(/5X,'RATHD1 EQUIPMENT NUMBER ', I2)
101   FORMAT(10X,'VOLUME = '1PE10.4,' CU FT ='1PE10.4,' GAL')
102   FORMAT(10X, 'RATE CONSTANTS (GMOLE/SEC CM SQ)+', /, 15X,
     *'CACO3=1,1PE11.4,' CASO4=',1PE11.4,' CASO3=',1PE11.4,'
     *LIMESTONE=',1PE11.4)
      IF(P(9).LE.0.) GO TO 50
      WRITE(6,110) P(10), P(11), P(12)
110   FORMAT(36X,'CRYSTAL AREA SPECIFIED'/10X,'CACO3=',1PE10.4,
     *5X,'CASO3*1/2H20=',1PE10.4,5X,'CASO4*2H20=',1PE10.4)
 50   CONTINUE
      RETURN 2
  1   CONTINUE
      CALL ADDER (LIS1,LIS2,LIS3,LIS4,LOS)
      IF(SV(LOS,49).LT.7.) SV(LOS,57)=1.E-10
      CALL TOLISP(LOS)
      SV(LOS,35)=SV(LOS,35)+SV(LOS,102)
      SV(LOS,117)=0.0
      SV(LOS,36)=SV(LOS,36)+SV(LOS,109)
      SV(LOS,39)=SV(LOS,39)+SV(LOS,102)+SV(LOS,109)
      DO 5 I=3,7,2
      XNN(I)=0.
      IL=(I-3)/2+2
      IF(P(9);GT.0.) SV(LOS,120+I)=P(8+IL)
      IF(SV(LOS,120+I).LE.0.) SV(LOS,120+I)=7500.
      ZSI(I)=VI(I)/SV(LOS,120+I)
  5   XNS(I)=SV(LOS,100+I)
      IOPT=2**20
      NS=1
      T=SV(LOS,5)
      CALL EQUILB(LOS,IOPT,T,PP,WNES,NS)
      NS=0
      IFLS=0
      DO 10 I=3,7,2
      IL=(I-3)/2+2
      RS(1,I)=EXP(APS(IL)-CKS(IL))
      IFLAG(I)=0
      IF(RS(1,I).LE.1.) GO TO 10
      APD(IL)=1000.*RS(1,I)   @SUBSATURATE METASTABLE SOLIDS

      IF(RS(1,I).LE.1.05*CV(I)) TO TO 10
      IFLAG(I)=1
      IFLS=1
      APD(IL)=CV(I)
 10   CONTINUE
```

```
      IF(IFLS.EQ.0) GO TO 11
      IF(RS(1,3).GT.CV(3)) SV(LOS,103)=SV(LOS,32)
      IF(RS(1,5).GT.CV(5)) SV(LOS,105)=SV(LOS,31)
      IF(RS(1,7).GT.CV(7)) SV(LOS,107)=SV(LOS,33)
      CALL EQUILB(LOS,IOPT,T,PP,WNES,NS)
      DO 12 I=3,7,2
      IL=(I-3)/2+2
      RS(2,I)=EXP(APS(IL)-CKS(IL))
      APD(IL)=1.
      IF(IFLAG(I).NE.1) GO TO 12
      XNN(I)=SV(LOS,100+I)
      WRITE(6,106) I,XNN(I)
  106 FORMAT(10X,'SOLID NO. ',I2,' GMOLES/S NUCLEATING',G12.6)
   12 CONTINUE
   11 CONTINUE
      DO 28 I=3,7,2
   28 SAG(I)=(SAPG(I)*XNN(I)+SV(LOS,120+I)*XNS(I))/(XNN(I)+XNS(I))
      CALL ADDER(LIS1,LIS2,LIS3,LIS4,LOS)
      IF(SV(LOS,49).LT.7.) SV(LOS,57)=1.E-10
      SV(LOS,35)=SV(LOS,35)-SV(LOS,101)
      SV(LOS,117)=0.0
      SV(LOS,36)=SV(LOS,36)-SV(LOS,108)
      DO 23 I=3,7,2
      XNI(I)=XNN(I)+XNS(I)
   23 CONTINUE
      V=28316.85*P(1)
   20 VRK(1)=P(2)*V*SAG(3)/1000.
      VRK(2)=P(4)*V*SAG(5)/1000.
      VRK(3)=P(3)*V*SAG(7)/1000.
      VRK(7)=P(8)*V*7.5
      J=0
      DO 21 I=3,7,2
      SV(LOS,100+I)=XNI(I)
   21 J=J+IFLAG(I)
      NRS=1
      IF(J.NE.0) NRS=2
      IF(RS(NRS,3).LE.1.) VRK(1)=0.
      IF(RS(NRS,5).LE.1.) VRK(2)=0.
      IR(RS(NRS,7).LE.1.) VRK(3)=0.
      DO 22 I=3,7,2
      IL=(I-3)/2+2
      IF(IFLAG(I).GT.1.OR.XNS(I).GT.0.) GO TO 22
      IF(I.EQ.3) VRK(1)=0.
      IF(I.EQ.5) VRK(2)=0.
      IF(I.EQ.7) VRK(3)=0.
      APD(IL)=1000.*RS(1,I)      @SUBSATURATE METASTABLE SOLIDS
   22 CONTINUE
      T = SV(LOS,5)
      CALL RATE (LOS,IOPT,T,PP,WNES,NS,VRK)
      DO 25 I=3,7,2
      IL=(I-3)/2+2
      ANO(I)=0.
      APD(IL)=1.
      IF(IFLAG(I).EQ.0) GO TO 29
      AI=((XNI(I)-XNN(I))*SV(LOS,120+I)+SAPG(I)*XNN(I))/XNI(I)
      PNM(I)=(SV(LOS,100+I)-XNI(I))*(XNN(I)*SAPG(I))/(AI*XNI(I))
      Z(I)=CLC(I)*((1.+PNM(I)/XNN(I))**.333)
      ANO(I)=VI(I)/Z(I)
   29 CONTINUE
      PSM(I)=SV(LOS,100+I)-XNI(I)-PNM(I)
      IF(PSM(I).LE.0.) PSM(I)=0.
      ZS(I)=ZSI(I)*((XNS(I)+PSM(I))/XNS(I))**.333
      ASO(I)=VI(I)/ZS(I)
   25 CONTINUE
      DO 26 I=3,7,2
   26 SAGT(I)=((XNN(I)+PNM(I))*ANO(I)+ASO(I)*(XNS(I)+PSM(I)))
     */SV(LOS,100+I)
      IFLS=0
      DO 27 I=3,7,2
      IF(ABS((SAGT(I)-SAG(I))/SAGT(I)).GT..0001) IFLS=1
   27 SAG(I)=SAGT(I)
      IF(IFLS.NE.0) GO TO 20
      WRITE(6.115)

  115 FORMAT(1H1)
      DO 30 I=3,7,2
      SV (LOS,120+I)=SAG(I)
      WRITE(6,105) I,ANO(I),SAG(I)
  105 FORMAT(/1X,'SOLID NO. ',I2,' OUTLET NUCLEI SURFACE AREA ',
     *G12.6,'(CM2/GM)'/2X,'AVERAGE PARTICLE SURFACE AREA ',
     *G12.6, '(CM2/GM)')
   30 CONTINUE
      CALL BOXCHK(0,0)
      RETURN 2
      END
```

3.3 System Balance Subroutines

The CTBAL1 subroutine is an overall mass balance routine used to assess cooling system water treatment requirements. The required inputs to the routine include complete specification of the ambient air, the air leaving the cooling tower, the drift, and the acid stream used for pH control. (The first three inputs are determined by CLGTR1.) Other inputs are the number of cycles of concentration, temperature change across the condenser, makeup water composition, and an acceptable range of $CaCO_3$ and $CaSO_4$ relative saturations.

CTBAL1 uses this input information to check the $CaCO_3$ relative saturation in the recirculating cooling water. If the $CaCO_3$ relative saturation is outside the acceptable range, the acid rate is adjusted by an iterative procedure to bring the $CaCO_3$ relative saturation within the range. Once the $CaCO_3$ condition is satisfied, the $CaSO_4$ relative saturation is checked. If it exceeds the desired value, which was specified as an input, chemical treatment is needed to lower the Ca^{++} concentration. The amount of Ca^{++} that must be removed is calculated, and this number is placed in a computer memory location that is in common with the chemical treatment routine CHMTRT, which is discussed in Section 3.2.

The CTBAL1 outputs include a complete specification of the blowdown stream leaving the cooling system, specification of the makeup water rate, specification of a new acid rate, and specification of the amount of calcium that must be removed in a water treatment step to keep the relative saturations of $CaCO_3$ and $CaSO_4$ in the desired ranges.

The PNDBAL subroutine is used in the ash sluicing model to perform an overall mass balance. This routine determines the plant effluent from the ash pond based on specified fly ash and fly ash sluice water, bottom ash and bottom ash sluice water, pond evaporation, the sludge solids content and the degree of carbon dioxide mass transfer between the pond liquor and the atmosphere. For all species except $CaSO_4$ solid-liquid equilibrium is assumed in the pond. $CaSO_4$ was allowed to remain supersaturated because evidence exists which indicate that it can remain supersaturated in an ash pond. For the recirculating ash sluicing simulations, this represents a worse case than the assumption of equilibrium which would cause Ca^{++} and $SO_4^{=}$ to be removed from the system.

There are three overall system balance subroutines, SYSTB1, SYSTB4, and SYSTB5, used in the scrubbing simulations for Four Corners and Colstrip. All of these subroutines perform overall material and energy balances. They calculate the amount of water vaporized in the scrubber, the makeup water flow rate and the flow rate and composition of the scrubber effluent stream. These subroutines have the option to not allow solids formation. These subroutines differ in the number of input and output streams that they consider. SYSTB1 has three input streams and two output streams. SYSTB4 has four input streams and two output streams. SYSTB5 has four input streams and three output streams. The choice of the correct subroutine is determined by the configuration of the system which is modeled.

4.0 CHEMICAL EQUILIBRIUM PROGRAM

The basis of the models used in this study is the chemical equilibrium program. This section presents a description of the program and the assumptions used to calculate the distribution of ionic species in aqueous systems. At the end of this section the nomenclature used in this description is presented.

4.1 Chemical Species

Inputs to the program are in the form of nine key species which are listed in Table 4-1. Here, the prefix "t" has been used to denote that these species are key or total species as opposed to gas, liquid, or solid species. For example, tCO_2 represents the total carbon dioxide species in the system. The total carbon dioxide species would consist of the sum of actual molecular and ionic species such as HCO_3^-, $CO_3^=$, $H_2CO_3(\ell)$, $CaCO_3(\ell)$, etc.

TABLE 4-1. EQUILIBRIUM PROGRAM KEY SPECIES

1.	tSO_2	6.	$tMgO$
2.	tCO_2	7.	tNa_2O
3.	tSO_3	8.	$tHCl$
4.	tN_2O_5	9.	tH_2O
5.	$tCaO$		

The chemical species which are considered significant in an aqueous system of these total species are listed in Table 4-2. These species are grouped according to liquid and solid species. Some species may exist as a liquid and as a solid, e.g., $CaCO_3$. Where ambiguity may arise, these species will be denoted using standard chemical notation. For example, calcium carbonate as a solid will be denoted by $CaCO_3(s)$. In writing algebraic equations (as opposed to chemical reaction equations), an abbreviated notation will frequently be used to avoid the use of numerous parentheses and brackets. In this abbreviated notation, solid calcium carbonate will be denoted by $sCaCO_3$ and dissolved or liquid calcium carbonate will be denoted by $\ell CaCO_3$.

TABLE 4-2. EQUILIBRIUM SPECIES

A: Liquid Species

1. H_2O
2. H^+
3. OH^-
4. HSO_3^-
5. $SO_3^=$
6. $SO_4^=$
7. HCO_3^-
8. $CO_3^=$
9. NO_3^-
10. HSO_4^-
11. H_2SO_3
12. H_2CO_3
13. Ca^{++}
14. $CaOH^+$
15. $CaSO_3$
16. $CaCO_3$
17. $CaHCO_3^+$
18. $CaSO_4$
19. $CaNO_3^+$
20. Mg^{++}
21. $MgOH^+$
22. $MgSO_3$
23. $MgHCO_3^+$
24. $MgSO_4$
25. $MgCO_3$
26. Na^+
27. $NaOH$
28. $NaCO_3^-$
29. $NaHCO_3$
30. $NaSO_4^-$
31. $NaNO_3$
32. Cl^-

B: Solid Species

1. $Ca(OH)_2$
2. $CaCO_3$
3. $CaSO_3$
4. $CaSO_3 \cdot \frac{1}{2}H_2O$
5. $CaSO_4$
6. $CaSO_4 \cdot 2H_2O$
7. $Mg(OH)_2$
8. $MgCO_3$
9. $MgCO_3 \cdot 3H_2O$
10. $MgCO_3 \cdot 5H_2O$
11. $MgSO_3$
12. $MgSO_3 \cdot 3H_2O$
13. $MgSO_3 \cdot 6H_2O$

All possible chemical species are not considered. For example, no solid nitrates are listed. Nitrates as a class are so soluble that within the range of interest of this program solid nitrates will not occur, so that the solubility relations for nitrates may be ignored. Nitrates need not be included in the solid equilibrium species.

4.2 System Equilibria

There are three types of equilibria which are considered in this program, liquid-liquid, gas-liquid, and solid-liquid. Liquid-liquid equilibria relate the activities of species within the liquid phase. Gas-liquid equilibria relate the activity of a liquid species to the equilibrium partial pressure of the corresponding gas species, i.e., the gas phase is assumed to behave ideally. Solid-liquid equilibria relate the activities of liquid species to the solubility product constant of the corresponding solid, i.e., the activities of the solid species are taken to be one.

Liquid-liquid and gas-liquid equilibria are different in that all terms in the liquid-liquid equilibria must enter into the mass balance relations given in Section 4.3, whereas the partial pressures of gases calculated with gas-liquid equilibria have not been related to the mass balances. In the case of solid-liquid equilibria, the quantity of solid does enter into the mass balance, but it does not enter into the solubility product expression. The presence of a solid depends on whether its solubility product is exceeded. If so, the quantity depends on the mass balance.

The chemical reactions which are considered and their associated equilibrium relations are given in Table 4-3. In the case of the solid-liquid equilibria, water of hydration (ν) must be assigned to some solids. The values of ν are functions of temperature according to the relative thermodynamic stability of the hydrates of each solid. Temperature ranges and hydrate numbers for each solid so treated are given in Table 4-4.

4.3 Material Balance

As stated in Section 4.2, the mass balances involve only the liquid and solid phases. The mass balance equations require that the actual molecular and ionic species in the liquid and solid phases be equal to the input total "key" species (see Section 4.1).

TABLE 4-3. EQUILIBRIUM RELATIONS

A: Liquid-Liquid Equilibria

Reaction	Equilibrium Relation	
$H_2O \rightleftarrows H^+ + OH^-$	$K_1\ \gamma(H_2O) = a(H^+)\ a(OH^-)$	(4.2-1)
$H_2SO_3 \rightleftarrows H^+ + HSO_3^-$	$K_2\ a(H_2SO_3) = a(H^+)\ a(HSO_3^-)$	(4.2-2)
$HSO_3^- \rightleftarrows H^+ + SO_3^=$	$K_3\ a(HSO_3^-) = a(H^+)\ a(SO_3^=)$	(4.2-3)
$HSO_4^- \rightleftarrows H^+ + SO_4^=$	$K_4\ a(HSO_4^-) = a(H^+)\ a(SO_4^=)$	(4.2-4)
$H_2CO_3 \rightleftarrows H^+ + HCO_3^-$	$K_5\ a(H_2CO_3) = a(H^+)\ a(HCO_3^-)$	(4.2-5)
$HCO_3^- \rightleftarrows H^+ + CO_3^=$	$K_5\ a(HCO_3^-) = a(H^+)\ a(CO_3^=)$	(4.2-6)
$CaOH^+ \rightleftarrows Ca^{++} + OH^-$	$K_7\ a(CaOH^+) = a(Ca^{++})\ a(OH^-)$	(4.2-7)
$CaSO_3 \rightleftarrows Ca^{++} + SO_3^=$	$K_9\ a(CaSO_3) = a(Ca^{++})\ a(SO_3^=)$	(4.2-8)
$CaCO_3 \rightleftarrows Ca^{++} + CO_3^=$	$K_9\ a(CaCO_3) = a(Ca^{++})\ a(CO_3^=)$	(4.2-9)
$CaHCO_3^+ \rightleftarrows Ca^{++} + HCO_3^-$	$K_{10}\ a(CaHCO_3^+) = a(Ca^{++})\ a(HCO_3^-)$	(4.2-10)
$CaSO_4 \rightleftarrows Ca^{++} + SO_4^=$	$K_{11}\ a(CaSO_4) = a(Ca^{++})\ a(SO_4^=)$	(4.2-11)
$CaNO_3^+ \rightleftarrows Ca^{++} + NO_3^-$	$K_{12}\ a(CaNO_3^+) = a(Ca^{++})\ a(NO_3^-)$	(4.2-12)
$MgOH^+ \rightleftarrows Mg^{++} + OH^-$	$K_{17}\ a(MgOH^+) = a(Mg^{++})\ a(OH^-)$	(4.2-13)
$MgSO_3 \rightleftarrows Mg^{++} + SO_3^=$	$K_{18}\ a(MgSO_3) = a(Mg^{++})\ a(SO_3^=)$	(4.2-14)
$MgHCO_3^+ \rightleftarrows Mg^{++} + HCO_3^-$	$K_{19}\ a(MgHCO_3^+) = a(Mg^{++})\ a(HCO_3^-)$	(4.2-15)
$MgSO_4 \rightleftarrows Mg^{++} + SO_4^=$	$K_{20}\ a(MgSO_4) = a(Mg^{++})\ a(SO_4^=)$	(4.2-16)
$MgCO_3 \rightleftarrows Mg^{++} + CO_3^=$	$K_{21}\ a(MgCO_3) = a(Mg^{++})\ a(CO_3^=)$	(4.2-17)
$NaOH \rightleftarrows Na^+ + OH^-$	$K_{25}\ a(NaOH) = a(Na^+)\ a(OH^-)$	(4.2-18)
$NaCO_3^- \rightleftarrows Na^+ + CO_3^=$	$K_{26}\ a(NaCO_3^-) = a(Na^+)\ a(CO_3^=)$	(4.2-19)
$NaHCO_3 \rightleftarrows Na^+ + HCO_3^-$	$K_{27}\ a(NaHCO_3) = a(Na^+)\ a(HCO_3^-)$	(4.2-20)
$NaSO_4^- \rightleftarrows Na^+ + SO_4^=$	$K_{28}\ a(NaSO_4^-) = a(Na^+)\ a(SO_4^=)$	(4.2-21)
$NaNO_3 \rightleftarrows Na^+ + NO_3^-$	$K_{29}\ a(NaNO_3) = a(Na^+)\ a(NO_3^-)$	(4.2-22)

B: Gas-Liquid Equilibria

Reaction	Equilibrium Relation	
$SO_2(g) + H_2O(\ell) \rightleftarrows H_2SO_3(\ell)$	$P(SO_2)\ \gamma(H_2O)\ K_2(SO_2) = a(H_2SO_3)$	(4.2-23)
$CO_2(g) + H_2O(\ell) \rightleftarrows H_2CO_3(\ell)$	$P(CO_2)\ \gamma(H_2O)\ K_2(CO_2) = a(H_2CO_2)$	(4.2-24)

C: Solid-Liquid Equilibria

Reaction	Equilibrium Relation	
$CaCO_3(s) \rightleftarrows Ca^{++} + CO_3^=$	$K_{sp}(CaCO_3) \geq a(Ca^{++})\ a(CO_3^=)$	(4.2-25)
$CaSO_4 \cdot 2H_2O(s) \rightleftarrows Ca^{++} + SO_4^= + 2H_2O(\ell)$	$K_{sp}(CaSO_4) \geq a(Ca^{++})\ a(SO_4^=)\ \gamma(H_2O)^2$	(4.2-26)
$CaSO_3 \cdot \frac{1}{2}H_2O(s) \rightleftarrows Ca^{++} + SO_3^= + \frac{1}{2}H_2O(\ell)$	$K_{sp}(CaSO_3) \geq a(Ca^{++})\ a(SO_3^=)\ \gamma(H_2O)^{\frac{1}{2}}$	(4.2-27)
$Ca(OH)_2(s) \rightleftarrows Ca^{++} + 2OH^-$	$K_{sp}[Ca(OH)_2] \geq a(Ca^{++})\ a(OH^-)^2$	(4.2-28)
$Mg(OH)_2(s) \rightleftarrows Mg^{++} + 2OH^-$	$K_{sp}[Mg(OH)_2] \geq a(Mg^{++})\ a(OH^-)^2$	(4.2-29)
$MgSO_3 \cdot \nu_1 H_2O(s) \rightleftarrows Mg^{++} + SO_3^= + \nu_2(H_2O)(\ell)$	$K_{sp}(MgSO_3) \geq a(Mg^{++})\ a(SO_3^=)\ \gamma(H_2O)^{\nu_1}$	(4.2-30)
$MgCO_3 \cdot \nu_2 H_2O(\ell) \rightleftarrows Mg^{++} + CO_3^= + \nu_2(H_2O)(\ell)$	$K_{sp}(MgCO_3) \geq a(Mg^{++})\ a(CO_3^=)\ \gamma(H_2O)^{\nu_2}$	(4.2-31)

TABLE 4-4. HYDRATE NUMBERS

Solid Species	Hydrate Number	Temperature Range
$MgSO_3 \cdot \nu_1 H_2O$	3	Greater than 38°C
	6	Less than 38°C
$MgCO_3 \cdot \nu_2 H_2O$	0	Greater than 100°C
	3	20°C to 100°C
	5	Less than 20°C

The mass balance equations for each total species are given in Table 4-5. The molar quantity (in gmoles) of each species [n(j)] is computed by multiplying the molality [m(j)] by the amount of liquid water (L_x) measured in kilograms. Here the index j is used to denote the actual molecular and ionic species in the liquid and solid phases.

Actually the mass balance relation for water is a hydrogen balance (Equation 4.3-9a). This balance equation is not used in the equilibrium program. A balance of the electrical charges, or an electroneutrality balance, is used instead. This balance is given in Table 4-5 by Equation 4.3-9b. This balance, like the water balance, reflects the fact that some hydrogen enters the system as HCl.

4.4 Constants

Two sets of constants are needed to implement this program. These are equilibrium constants and the constants for the activity coefficient correlation. Equilibrium constants are discussed in Section 4.4.1 and activity coefficients in Section 4.4.2.

4.4.1 Equilibrium Constants

The relation for calculating equilibrium constants is given in Equation 4.4-1.

TABLE 4-5. MASS BALANCES

$$\begin{aligned} n(tSO_2) = {} & n(HSO_3^-) + n(SO_3^=) + n(\ell H_2SO_3) + n(\ell CaSO_3) \\ & + n(\ell MgSO_3) + n(sCaSO_3 \cdot \tfrac{1}{2}H_2O) + n(sMgSO_3 \cdot \nu_1 H_2O) \end{aligned} \tag{4.3-1}$$

$$\begin{aligned} n(tCO_2) = {} & n(HCO_3^-) + n(CO_3^=) + n(\ell H_2CO_3) + n(\ell CaCO_3) \\ & + n(CaHCO_3^+) + n(MgHCO_3^+) + n(\ell MgCO_3) + n(NaCO_3^-) \\ & + n(\ell NaHCO_3) + n(sCaCO_3) + n(sMgCO_3 \cdot \nu_2 H_2O) \end{aligned} \tag{4.3-2}$$

$$\begin{aligned} n(tSO_3) = {} & n(SO_4^=) + n(HSO_4^-) + n(\ell CaSO_4) + n(NaSO_4^-) \\ & + n(sCaSO_4 \cdot 2H_2O) \end{aligned} \tag{4.3-3}$$

$$n(tN_2O_5) = \tfrac{1}{2}[n(NO_3^-) + n(CaNO_3^+) + n(\ell NaNO_3)] \tag{4.3-4}$$

$$\begin{aligned} n(tCaO) = {} & n(Ca^{++}) + n(CaOH^+) + n(\ell CaSO_3) + n(\ell CaCO_3) \\ & + n(CaHCO_3^+) + n(\ell CaSO_4) + n(CaNO_3^+) + n(sCaCO_3) \\ & + n(sCaSO_4 \cdot 2H_2O) + n(sCaSO_3 \cdot \tfrac{1}{2}H_2O) + n[sCa(OH)_2] \end{aligned} \tag{4.3-5}$$

$$\begin{aligned} n(tMgO) = {} & n(Mg^{++}) + n(MgOH^+) + n(\ell MgSO_3) + n(MgHCO_3^+) \\ & + n(\ell MgCO_3) + n(\ell MgSO_4) + n[sMg(OH)_2] \\ & + n(sMgCO_3 \cdot \nu_2 H_2O) + n(sMgSO_3 \cdot \nu_1 H_2O) \end{aligned} \tag{4.3-6}$$

$$\begin{aligned} n(tNa_2O) = {} & \tfrac{1}{2}[n(Na^+) + n(\ell NaOH) + n(NaCO_3^-) + n(\ell NaHCO_3) \\ & + n(NaSO_4^-) + n(\ell NaNO_3)] \end{aligned} \tag{4.3-7}$$

TABLE 4-5. MASS BALANCES (Continued)

$$n(tHCl) = n(Cl^-) \qquad (4.3\text{-}8)$$

$$\begin{aligned} n(tH_2O) = {} & n(\ell H_2O) + \tfrac{1}{2}[n(H^+) + n(OH^-) + n(HSO_3^-) + n(HSO_4^-) \\ & + n(HCO_3^-) + n(CaOH^+) + n(CaHCO_3^+) + n(MgOH^+) \\ & + n(MgHCO_3^+) + n(\ell NaOH) + n(\ell NaHCO_3^+)] \\ & + n(\ell H_2CO_3) + n(\ell H_2SO_3) + n[sCa(OH)_2 \ + n\ sMg(OH)_2] \\ & + \tfrac{1}{2}\ n(sCaSO_3 \cdot \tfrac{1}{2}H_2O) + 2\ n(sCaSO_4 \cdot 2H_2O) \\ & + \nu_1\ n(sMgSO_3 \cdot \nu_1 H_2O) + \nu_2\ n(sMgCO_3 \cdot \nu_2 H_2O) \\ & - \tfrac{1}{2}\ n(tHCl) \qquad (4.3\text{-}9a) \end{aligned}$$

$$\begin{aligned} & n(H^+) + 2\ n(Ca^{++}) + n(CaOH^+) + n(CaHCO_3^+) + n(CaNO_3^+) + 2\ n(Mg^{++}) \\ & + n(MgOH^+) + n(MgHCO_3^+) + n(Na^+) = n(OH^-) + n(HSO_3^-) \\ & + 2\ n(SO_3^=) + 2\ n(SO_4^=) + n(HCO_3^-) + 2\ N(CO_3^=) + n(NO_3^-) \\ & + n(HSO_4^-) + n(NaCO_3^-) + n(NaSO_4^-) + n(Cl^-) \qquad (4.3\text{-}9b) \end{aligned}$$

$$\log_{10}(K) = -A_x/T - B_x \log_{10} T - C_x T + D_x \qquad (4.4\text{-}1)$$

where T is the Kelvin temperature and A_x, B_x, C_x, and D_x are constants. Constants for these chemical reactions are stored in the chemical equilibrium program.

4.4.2 Activity Coefficients

The activity coefficients are correlated with the ionic strength (I) of the solution. This quantity is related to the molality (m) and charge (z) of all the species in solution by Equation 4.4.-2.

$$I = \tfrac{1}{2} \sum_{j\ell} m(j\ell)\ z(j\ell)^2 \qquad (4.4\text{-}2)$$

For ionic species, the logarithm of the activity coefficients is correlated with ionic strength by Equation 4.4-3.

$$\log_{10}[\gamma(j\ell)] = A\ z(j\ell)^2\ \frac{-I^{\frac{1}{2}}}{1 + Ba^{o}(j\ell)I^{\frac{1}{2}}} + b(j\ell)\ I \qquad (4.4\text{-}3)$$

Here, A and B are temperature-dependent constants for the mixture.

$$A = 1.8248 \cdot 10^{3}/(DT)^{3/2} \qquad (4.4\text{-}4)$$

$$B = 50.292/(DT)^{\frac{1}{2}} \qquad (4.4\text{-}5)$$

where D is the dielectric constant of water in cgs units and T is the Kelvin temperature. The other constants in Equation 3.2-2 are parameters for each ionic species. Values for these are stored within the equilibrium program.

In the case of uncharged species, the activity coefficient is determined by Equation 4.4-6.

$$\log_{10}[\gamma(j\ell)] = 0.076\ I \qquad (4.4\text{-}6)$$

4.5 Makeup Water Adjustment

Grab samples of many of the streams studied were taken and analyzed for calcium, magnesium, sodium, chloride, carbonates, nitrate, sulfate, and sulfite. This subsection describes how the data for the makeup water were modified for use in the cooling tower and scrubbing models.

Prior to the initiation of the cooling system simulations, the makeup water compositions were altered slightly from the sample values. This was done in an effort to reduce the residual electroneutrality which may result from analytical inaccuracies. The residual electroneutrality is a parameter computed in the aqueous ionic equilibrium program. It is defined as the total positive charges in solution minus the total negative charges. When using the equilibrium program to evaluate analytical accuracy, the measured pH is specified and a residual electroneutrality is computed. If this charge imbalance is significant when compared to the total charge (sum of the absolute values) in the solution, then analytical inaccuracies are indicated.

When the equilibrium program is employed in a process simulation, the residual electroneutrality is minimized and the stream pH is calculated. When the equilibrium program is used in this way, analytical errors can have significant impact on the pH of an unbuffered liquor such as the makeup water stream. The composition of the makeup water was altered slightly to generate a solution pH similar to the measured pH when the residual electroneutrality was minimized. That is why there is some deviation between the compositions measured at the plants and the compositions used in the simulations. It should also be noted that silica was not included in the electroneutrality balances.

The changes made are presented in Tables 4-6 through 4-10. These tables present the composition changes required for the five plants studied.

TABLE 4-6. MONTOUR MAKEUP WATER COMPOSITION ADJUSTMENTS

	Sample mg/ℓ	Balanced mg/ℓ
Calcium (Ca^{++})	28.4	28.4
Magnesium (Mg^{++})	5.5	5.5
Sodium (Na^{+})	8.5	8.1
Chloride (Cl^{-})	19.0	22.0
Carbonates ($CO_3^{=}$)	6.0	6.0
Nitrate (NO_3^{-})	5.5	5.5
Sulfate ($SO_4^{=}$)	67.0	67.0
Residual Electroneutrality	1.7×10^{-6}	-1.5×10^{-9}
pH	8.1	8.1
Relative Saturation		
$CaCO_3$	0.013	0.013
$CaSO_4 \cdot 2H_2O$	0.012	0.012

TABLE 4-7. COLSTRIP MAKEUP WATER COMPOSITION ADJUSTMENTS

	Sample mg/ℓ	Balanced mg/ℓ
Calcium	39.9	39.9
Magnesium	10.7	10.7
Sodium	57.3	40.3
Chloride	17.0	17.0
Carbonates (as $CO_3^=$)	6.0	6.0
Nitrate (as NO_3^-)	1.4	1.4
Sulfate (as $SO_4^=$)	188.0	188.0
Residual Electroneutrality	6.6×10^{-4}	-7.6×10^{-10}
pH	10.3	10.5
Relative Saturation		
$CaCO_3$	1.08	0.91
$CaSO_4 \cdot 2H_2O$	0.034	0.039

TABLE 4-8. FOUR CORNERS MAKEUP WATER COMPOSITION ADJUSTMENTS

	Sample mg/ℓ	Balanced mg/ℓ
Calcium (Ca^{++})	160.	160.
Magnesium (Mg^{++})	40.	40.
Sodium (Na^+)	218.	189.
Chloride (Cl^-)	110.	135.
Carbonates ($CO_3^=$)	77.	77.
Nitrate (NO_3^-)	9.	9.
Sulfate ($SO_4^=$)	680.	680.
Residual Electroneutrality	1.7×10^{-3}	3.0×10^{-8}
pH	8.1	8.4
Relative Saturation		
$CaCO_3$	1.2	2.6
$CaSO_4 \cdot 2H_2O$	0.21	0.21

TABLE 4-9. COMANCHE MAKEUP WATER COMPOSITION ADJUSTMENTS

	Sample mg/ℓ	Balanced mg/ℓ
Calcium (Ca^{++})	36.5	36.5
Magnesium (Mg^{++})	10.2	10.2
Sodium (Na^{+})	19.0	26.2
Chloride (Cl^{-})	9.0	5.3
Carbonates ($CO_3^{=}$)	6.0	5.4
Nitrate (NO_3^{-})	9.0	12.4
Sulfate ($SO_4^{=}$)	163.0	163.2
Residual Electroneutrality	-3.6×10^{-4}	2.7×10^{-9}
pH	6.2	6.9
Relative Saturation		
$CaCO_3$	1×10^{-4}	9.4×10^{-4}
$CaSO_4 \cdot 2H_2O$	0.028	0.027

TABLE 4-10. BOWEN MAKEUP WATER COMPOSITION ADJUSTMENTS

	Sample mg/ℓ	Balanced mg/ℓ
Calcium (Ca^{++})	6.1	6.0
Magnesium (Mg^{++})	1.7	1.7
Sodium (Na^{+})	1.4	1.4
Chloride (Cl^{-})	2.1	2.1
Carbonates ($CO_3^{=}$)	20.4	20.4
Nitrate (NO_3^{-})	4.0	4.3
Sulfate ($SO_4^{=}$)	1.9	1.9
Residual Electroneutrality	-3.3×10^{-5}	-1.1×10^{-8}
pH	7.7	7.8
Relative Saturation		
$CaCO_3$	0.016	0.02
$CaSO_4 \cdot 2H_2O$	1.0×10^{-4}	9.4×10^{-5}

NOMENCLATURE

a	activity
a^o	activity coefficient correlation parameter
A	activity coefficient correlation parameter
A_x	equilibrium constant correlation parameter
b	activity coefficient correlation parameter
B	activity coefficient correlation parameter
B_x	equilibrium constant correlation parameter
C_x	equilibrium constant correlation parameter
D	dielectric constant of water
D_x	equilibrium constant correlation parameter
g	designation for gas species
I	ionic strength
K_n	liquid-liquid equilibrium constant, where n is the reaction index number
K_p	gas-liquid equilibrium constant
K_{sp}	solubility product constant
ℓ	designation for liquid species
m	molality
n	molar flow rate
P	partial pressure
s	designation for solid species
t	designation for total species
T	Kelvin temperature
z	species charge

Greek

γ	activity coefficient
ν	hydration number

Appendix F. Recycle/Reuse Options at Four Corners (Arizona Public Service)

1.0 INTRODUCTION

This appendix describes the analysis of the scrubbing system at the Arizona Public Service Four Corners Station under EPA Contract No. 68-03-2339, Water Recycle/Reuse Alternatives in Coal-Fired Steam-Electric Power Plants. The results of the computer modeling performed for existing operations and for the recycle/reuse alternatives, with rough cost estimates for the technically feasible options are discussed.

1.1 Summary

Three major topics are discussed in this appendix:

1) Existing Operations Modeling,
2) Alternatives Modeling, and
3) Economics.

The results of the existing operations simulations compare well to the sample data obtained at the plant. Potential scaling conditions were found at several points in the scrubbing system for low (2%) solids operation. The scrubber effluent, thickener overflow, and thickener underflow all were identified as showing $CaSO_4 \cdot 2H_2O$ relative saturations above 1.3, indicating a tendency to form gypsum scale. No calcium carbonate scaling was noted. A simulation of high (9%) solids operation showed increased scaling potential in the system.

Four alternatives were investigated for the particulate scrubbing system at Four Corners. Table 1-1 presents a summary of these four alternatives compared to existing operations.

The results of the first alternative simulation indicate that the present system tankage capacity is not sufficient to allow ample gypsum precipitation to prevent scaling.

In the second alternative, a tank capacity of 37,500 cubic meters (1.33 x 10^6 cubic feet) was simulated. Gypsum relative saturations were reduced to levels below the critical level required for the onset of scaling. Two cases were studied with different scrubber liquid-to-gas ratios (L/G). The existing L/G of 4.7 ℓ/m^3 @ STP (35.2 gal/1000scf) gave a scrubber bottoms pH of 2.9 and an L/G of 10.0 ℓ/m^3 @ STP (74.8 gal/1000 scf) gave a pH of 3.9 (assuming 50% SO_2 removal), indicating that higher L/G's are desirable for corrosion control.

TABLE 1-1. SUMMARY OF RECYCLE/REUSE OPTIONS AT FOUR CORNERS[1]

	Existing Condition		Alternative Two		Alternative Three		Alternative Four
	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2	Case 1
Weight Percent Solids in Thickener Bottoms	10	30	30	30	30	30	30
Hold Tank Volume, m^3 (ft^3)	0	0	37,500 (1.33×10^6)	37,500 (1.33×10^6)	37,500 (1.33×10^6)	21,200 (0.75×10^6)	8900 (0.31×10^6)
Liquid to Gas Ratio, ℓ/m^3 @ STP (gal/scf)	4.7 (35.2)	4.7 (35.2)	4.7 (35.2)	10.0 (74.8)	10.0 (74.8)	10.0 (74.8)	10.0 (74.8)
% Recycle from the Ash Pond	0	0	0	0	28	28	0
SO_2 Removal, %	30	30	50	50	50	50	50
Oxidation, %	98.6	98.6	98.6	98.6	98.6	98.6	98.6
Particulate Removal prior to scrubber, %	None	None	None	None	None	None	60
Scrubber Makeup Rate, ℓ/sec (GPM)	223 (3540)	70.7 (1730)	70.7 (1120)	70.7 (1120)	50.8 (805)	50.8 (805)	41.0 (650)
Costs:[2]							
Capital, 1976 $	--	--	3,334,000	4,275,000	4,328,000	3,317,000	3,385,000
Operating, 1976 $[3] (mils/kWh)	--	--	628,000 (.128)	1,101,000 (.225)	1,109,000 (.226)	958,000 (.195)	968,000 (.198)

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[1] Alternative One is not included because it was not deemed technically feasible due to high $CaSO_4$ relative saturations in the SO_2 scrubber.

[2] These rough cost estimates were made to compare technically feasible options and do not include a "difficulty to retrofit" factor.

[3] Includes capital amortization at 15% per year

The third alternative simulation, recycling the ash pond overflow to the scrubbing system, indicated that the pond overflow has no major impact on the gypsum relative saturations in the system but reduces the water makeup requirements from 70.7 ℓ/sec (1122 GPM) for Alternative 2 to about 50.8 ℓ/sec (807 GPM). Also, a simulation with ash pond overflow recycle using a reaction tank volume of 21,200 m^3 (7.5×10^5 ft^3) showed that a more reasonable reaction tank volume can be utilized. This simulation showed a gypsum relative saturation of 1.19 in the scrubber effluent slurry.

The fourth alternative shows that reaction tank volume may be decreased further by removing a portion of the fly ash by dry methods prior to the scrubbing system. A volume of 8900 m^3 (3.14×10^5 ft^3) was used to obtain a gypsum relative saturation of 1.19 in the scrubber effluent (60% of fly ash removed prior to scrubber). Water makeup requirements were also reduced to 41.0 ℓ/sec (650 GPM).

All of these alternatives assumed 98.6% oxidation of the SO_2 sorbed in the scrubbers. Process modification may cause the oxidation to decrease, thereby decreasing the reaction tank volumes necessary to prevent scale. Since less $CaSO_4 \cdot 2H_2O$ is formed, the reaction time required to form gypsum is also decreased. Modifications made after this study was completed decreased the oxidation at Four Corners so that all of the sulfate formed coprecipitated with calcium sulfite (<15% oxidation). Lime was added to the sump below the venturi to increase SO_2 removal. The resulting higher pH liquors apparently reduced the oxidation.

The rough-cost estimates of the technically feasible options (Alternatives 2-4) indicate that three to four million dollars would be required to upgrade the particulate scrubbing system so that scale potential is eliminated and water requirements reduced. The least expensive alternative was Alternative 3, case two (recycle ash pond overflow, reduced reaction tank volume), followed closely by the fourth option. Alternative 2, cases one and two, and Alternative 3, case one showed similar installed costs. Energy consumption did not vary radically among alternatives, although Alternative 2, case one (increased tank volume, low L/G) indicated a lower energy requirement was necessary and therefore less operating costs.

Detailed discussions of the existing operations simulations, the alternative simulations, and the rough cost estimates constitute the main body of this appendix.

2.0 PLANT CHARACTERISTICS

The Arizona Public Service Company (APS) Four Corners Plant is a five-unit 2,150 Mw coal-fired electric generating station located near Farmington, New Mexico. The coal utilized at Four Corners is approximately 20% ash and 0.5 - 1.0% sulfur with a heating value of about 9,300 Btu/lb. The plant uses a cooling pond and bottom ash wet sluicing for all units, particulate wet scrubbing for Units 1-3, and electrostatic precipitators for Units 4 and 5 (dry ash disposal).

This section of the appendix describes the characterization of the Four Corners plant's water system including the cooling, ash sluicing, and wet scrubbing systems. First, an overall water balance for the plant is presented which shows the major in-plant water flows and chemical analyses for the streams which were sampled. Then a detailed description of each of the major water consumers in the plant is given. This is followed by a discussion of the simulation basis for modeling operations at the Four Corners plant. Finally, the computer simulation results are presented and discussed. This discussion will include a comparison of the simulation results and the chemical analyses of the samples taken. Areas exhibiting scale potential will be identified.

2.1 Water Balance

A schematic of the Four Corners plant water system is shown in Figure 2-1. The major streams are shown for the particulate scrubbing system and bottom ash sluicing systems. Makeup water for the plant (Stream 18) is taken from the San Juan River and stored in Morgan Lake, which serves as the source for all water used in the system. A periodic blowdown (Stream 17) is taken from Morgan Lake to control the total dissolved solids concentration. This blowdown is discharged to the Chaco River which flows into the San Juan River.

Cooling water, bottom ash sluicing water, boiler makeup water, and makeup water for the particulate scrubbing system are taken from Morgan Lake. In addition to the blowdown stream from Morgan Lake, water leaves the plant through evaporation from Morgan Lake, evaporation from the ash pond, evaporation in the scrubbers, and ash pond overflow. Some vaporization also occurs in bottom ash sluicing operations due to the high ash temperature.

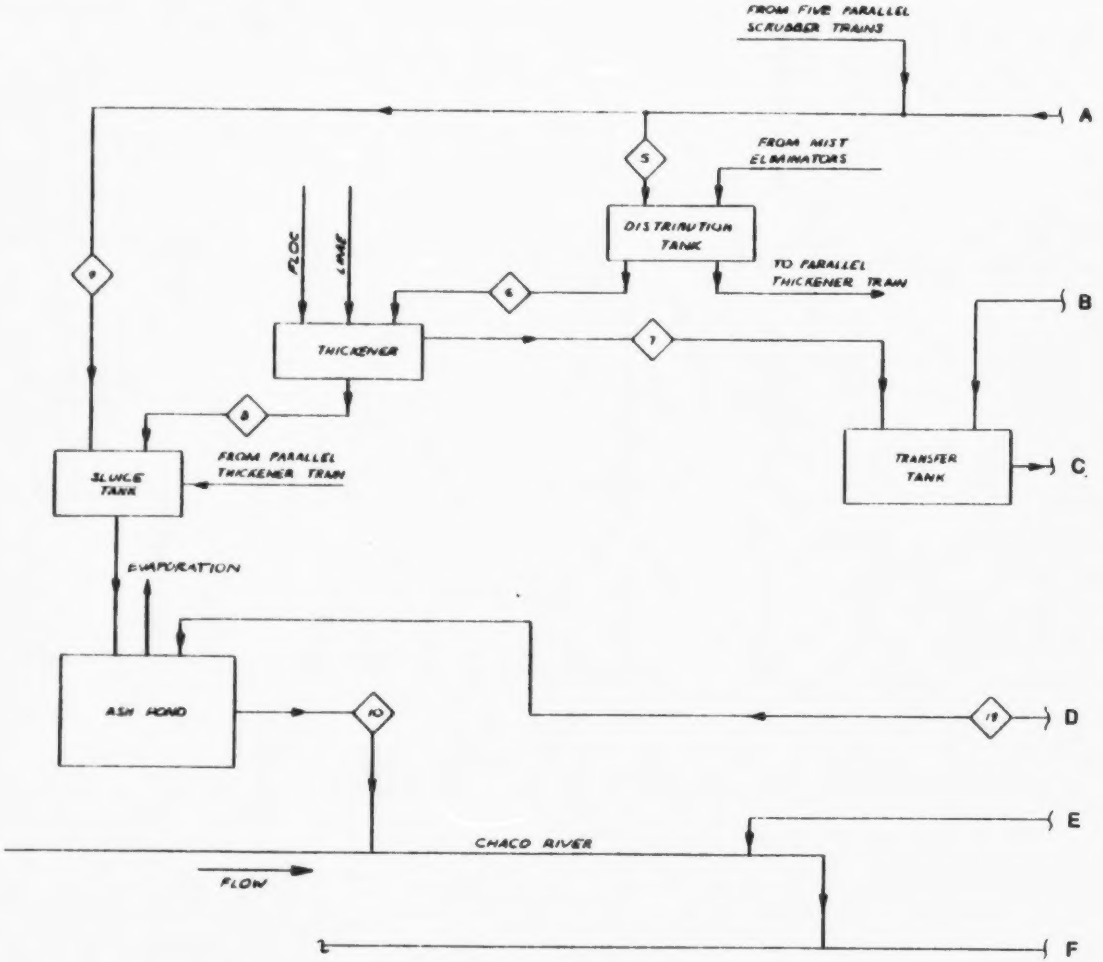

Figure 2-1. Arizona Public Service Four Corners Station water balance. (Sheet 1 of 3)

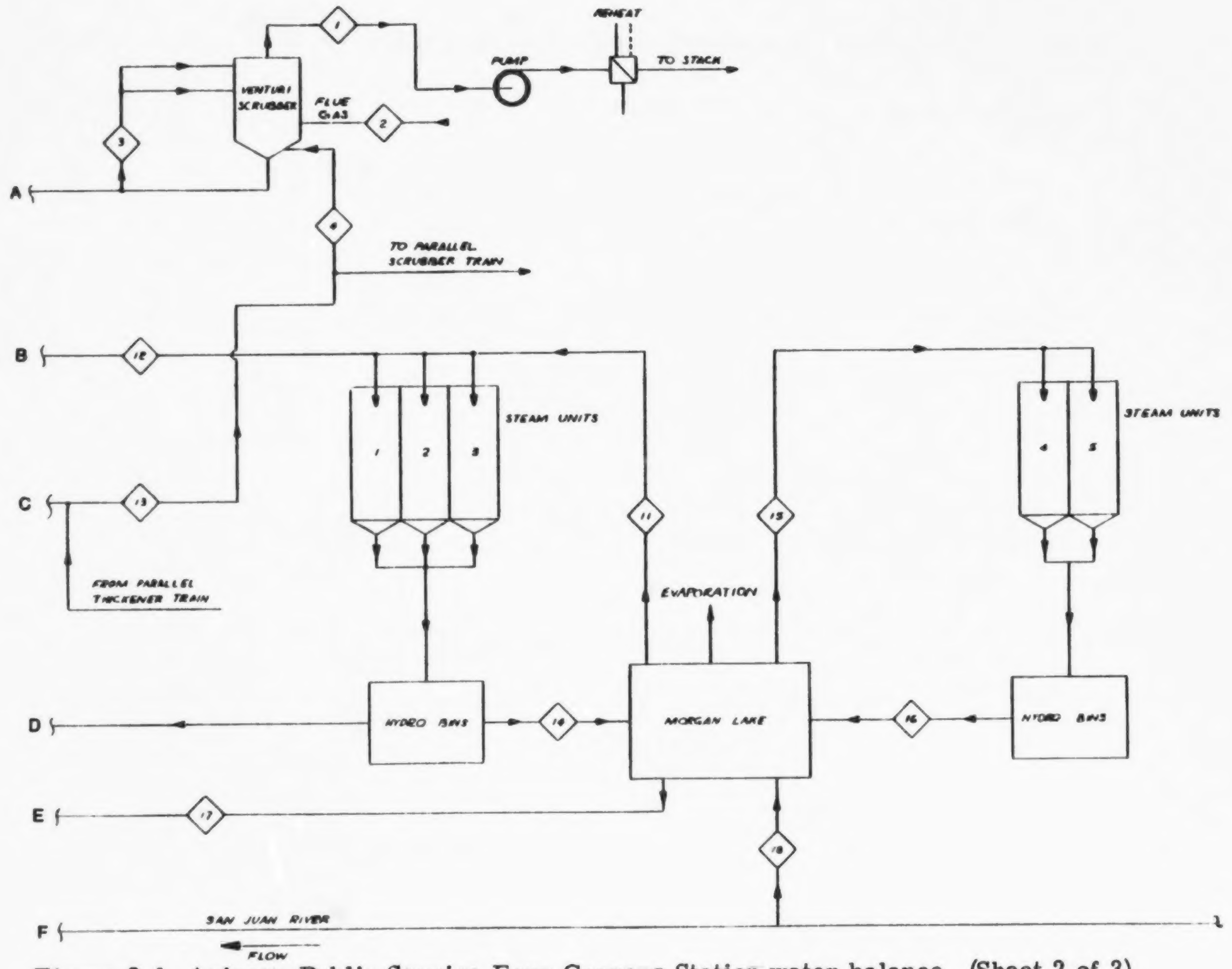

Figure 2-1. Arizona Public Service Four Corners Station water balance. (Sheet 2 of 3)

Stream Number	1	2	3	4	5	6	7	8	9	10
Stream Name	Stack Gas	Flue Gas	Scrubber Recycle	Scrubber Makeup	Distribution Tank Feed	Thickener Feed	Thickener Overflow	Thickener Underflow	Sluice Tank Feed	Ash Pond Overflow
Flow: Metric	588,000 m³/hr (744,000)	692,000 m³/hr (875,000)	434 ℓ/sec (550)	131 ℓ/sec (162)	746 ℓ/sec	380 ℓ/sec	375 ℓ/sec	5 ℓ/sec	64 ℓ/sec	69 ℓ/sec
Flow: English	346,000 acfm* (438,000)	407,000 acfm* (515,000)	6880 gpm* (8720)	2070 gpm* (2565)	11,830 gpm	6029 gpm	5950 gpm	80 gpm	1010 gpm	1100 gpm
pH			2.8 (3.1)		2.8	2.8	3.8	8.3	2.8	9.0
Calcium			790 (670)		790	790	730	330	790	650
Magnesium			49 (66)		49	49	54	38	49	44
Sodium			290 (350)		290	290	320	280	290	280
Potassium			11 (14)		11	11	14	8	11	10
Chloride			160 (220)		160	160	180	110	160	180
Carbonate(As CO_3)			30 (27)		30	30	16	60	30	29
Sulfate(As SO_4)			2740 (2930)		2740	2740	2540	1160	2740	2040
Sulfite(As SO_3)			8 (60)		8	8	18		8	
Nitrate(As NO_3)			25 (47)		25	25	24	7	25	23
Phosphate(As PO_4)			2.2 (3.5)		2.2	2.2	<0.3	<0.3	2.2	<0.3
Silicates(As SiO_3)			270 (360)		270	270	140	150	270	730
Suspended Solids			2.2 (8.8)		2.2	2.2	0.06	10.0	2.2	<0.01
Dissolved Solids			4370 (4690)		4370	4370	4110	1760	4370	3880

Stream Number	11	12	13	14	15	16	17	18	19
Stream Name	Makeup to Units 1,2,&3	Makeup to Transfer Tank	Transfer Tank Effluent	Bottom Ash Sluice From Units 1,2,&3	Makeup to Units 4&5	Bottom Ash Sluice From Units 4&5	Blowdown from Morgan Lake	Makeup to Morgan Lake	Bottom Ash Sluice to Ash Pond
Flow: Metric English	197 ℓ/sec 3120 gpm	129 ℓ/sec 2040 gpm	851 ℓ/sec 13490 gpm	40 ℓ/sec . 640 gpm	95 ℓ/sec 1500 gpm	95 ℓ/sec 1500 gpm	115 ℓ/sec 1820 gpm	940 ℓ/sec 15000 gpm	25 ℓ/sec 396 gpm
pH	8.1	8.1		6.9	8.1		8.1	7.7	6.9
Calcium	160	160		160	160		160	55	160
Magnesium	40	40		35	40		40	10	35
Sodium	210	210		210	210		210	37	210
Potassium	8	8		8	8		8	2	8
Chloride	110	110		140	110		110	8.5	140
Carbonate(As CO_3)	77	77		74	77		77	116.4	74
Sulfate(As SO_4)	680	680		690	680		680	117.6	690
Sulfite (As SO_3)									
Nitrate(As NO_3)	9	9			9		9	1	
Phosphate(As PO_4)	<0.3	<0.3		<0.3	<0.3		<0.3		<0.3
Silicates(As SiO_3)	100	100		110	100		100	119	110
Suspended Solids	<0.01	<0.01			<0.01		<0.01		
Dissolved Solids	1350	1305		1420	1350		1350	350	1420

* Numbers in parentheses refer to Unit 3 scrubber trains, other numbers are for Unit 1 or 2 trains.

Figure 2-1. Arizona Public Service Four Corners Station water balance. (Sheet 3 of 3)

This study deals primarily with the particulate wet scrubbing system and subsequent ash disposal for Units 1-3. Since water is recycled in the cooling and bottom ash sluicing systems there is little potential for water recycle-reuse alternatives in these systems. Also, scaling problems have been encountered in the scrubbing system and the study of recycle/reuse alternatives at Four Corners dictates addressing the causes and potential solutions to these problems.

Streams which are not shown in Figure 2-1 include the cooling water which circulates between Morgan Lake and the condensers for each unit, boiler makeup water, and water treatment wastes. Boiler makeup water is taken from Morgan Lake after it is passed through water treatment and evaporators. Water-treating wastes recycled to Morgan Lake for October, 1975, totaled about 1.8×10^9 ℓ (4.8×10^8 gal), including evaporator and demineralizer wastes.

Since Morgan Lake has been deemed a navigable waterway, these water treatment wastes along with general plant drainage present a problem. However, these wastes may be discharged to the ash pond, preventing any contamination of Morgan Lake through the addition of dissolved solids. The impact of this process change on the results of this study which primarily concerns the scrubbing system will be minimal. The results of the simulations which involve ash pond overflow recycle will not be adversely affected since the ash pond will already be saturated with respect to calcium sulfite, calcium carbonate, and calcium sulfate and any addition of these ions will only cause increased precipitation in the pond. In addition, the ash pond overflow only provides 28% of the total scrubbing system makeup water. The operation of the scrubbing system with respect to scaling will therefore not be adversely affected by the addition of water treating wastes to the ash pond.

The level of suspended solids in Morgan Lake due mainly to bottom ash sluicing operations is not addressed in this study. The focus of this study is on the chemical aspects of water recycle/reuse alternatives at Four Corners.

Additional streams not shown in Figure 2-1 are the evaporation from Morgan Lake and the ash pond. During October, 1975, about 1.6×10^9 ℓ (4.2×10^8 gal) was evaporated from Morgan Lake and 2.1×10^7 ℓ (5.5×10^6 gal) was evaporated from the ash pond. Also, seepage from Morgan Lake during October, 1975, was about 4.8×10^7 ℓ (1.3×10^7 gal). The influent rate from the San Juan River to Morgan Lake was 2.9×10^9 ℓ (7.7×10^8 gal) while the blowdown from the lake was 7.3×10^8 ℓ (1.9×10^8 gal).

All of the flows for the particulate scrubbing are design values reported by APS. The remaining stream flow rates are average values calculated from data supplied by APS over the period January to December 1975. Table 2-1 presents the values reported on a monthly basis. In most cases the flows measured in November are very close to the average for the year. The two streams with the largest variation are the makeup and blowdown streams from Morgan Lake. This is because Morgan Lake acts as a large surge tank for the Four Corners Plant and makeup and blowdown requirements are determined by a combination of factors. The TDS and species concentrations for each stream were taken from sample data taken at the plant in November of 1975. A more detailed description of the samples taken and analytical procedures used is presented in Appendix B.

Calculated parameters for the sampled streams are presented in Table 2-2. Included are the relative saturations of $CaCO_3$, $CaSO_4$ and $Mg(OH)_2$ as well as the partial pressure of CO_2 and the % residual electroneutrality. These parameters are useful for characterization of the individual streams.

The relative saturation is a parameter which indicates the potential of a stream to produce scale. When the relative saturation is greater than the critical value, solids formation can be expected. The critical values for the three species reported in Table 2-2 are 2.5 for $CaCO_3$, 3.4 for $Mg(OH)_2$, and 1.3 - 1.4 for $CaSO_4 \cdot 2H_2O$. The relative saturations of $CaCO_3$ only show a tendency for solid formation in the thickener underflow and the ash pond. $CaSO_4 \cdot 2H_2O$ relative saturations are all near the critical value with the exception of the makeup water, the thickener underflow and the bottom ash sluice. This is not surprising since gypsum scale is a serious problem at Four Corners.

The equilibrium partial pressure of CO_2 above the streams sampled at Four Corners is also presented in Table 2-2. The partial pressure of CO_2 in the atmosphere is 3.3×10^{-4} atm. Most of the streams have partial pressures of CO_2 near atmospheric. The scrubber liquor seems to be high in dissolved

TABLE 2-1. MONTHLY VARIATION OF FLOWS FROM SELECTED STREAMS AT FOUR CORNERS*

Stream Name	Stream Number	Ave	Jan	Feb	Mar	April	May	June	July	Aug	Sept	Oct	Nov	Dec
Sluice Tank Feed	9	63.9 (1013)	65.5 (1038)	53.2 (843)	65.7 (1041)	64.4 (1021)	64.1 (1016)	64.8 (1027)	64.8 (1027)	65.1 (1032)	64.6 (1024)	64.2 (1018)	64.4 (1021)	65.5 (1038)
Ash Pond Overflow	10	69.1 (1095)	15.3 (243)	51.0 (808)	83.6 (1325)	91.9 (1457)	74.2 (1176)	62.2 (986)	96.5 (1530)	70.7 (1121)	66.0 (1046)	61.0 (967)	98.1 (1555)	55.2 (875)
Makeup to Units 1, 2 and 3	11	197 (3123)	214 (3392)	--	--	--	--	--	--	--	--	180 (2853)	--	--
Makeup to Transfer Tank	12	129 (2045)	132 (2092)	--	--	--	--	--	--	--	--	127 (2013)	--	--
Bottom Ash Sluice from Units 1, 2 and 3	14	40.4 (640)	82.2 (1303)	76.6 (1214)	21.9 (347)	0 (0)	59.2 (938)	42.4 (672)	60.0 (951)	61.8 (980)	0 (0)	53.0 (840)	28.1 (445)	0 (0)
Makeup to Units 4 and 5	15	95.3 (1511)	119.4 (1893)	100.7 (1596)	79.8 (1265)	--	--	46.1 (731)	73.9 (1171)	133.2 (2111)	103.8 (1645)	87.6 (1389)	92.8 (1471)	114.4 (1813)
Bottom Ash Sluice from Units 4 and 5	16	94.7 (1501)	118.2 (1874)	99.7 (1580)	79.0 (1252)	--	--	44.2 (701)	73.9 (1171)	134.5 (2132)	102.7 (1628)	86.7 (1374)	88.9 (1409)	113.3 (1796)
Blowdown from Morgan Lake	17	114.5 (1815)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	271.8 (4308)	278.7 (4418)	272.0 (4311)	272.0 (4311)	272.0 (4311)
Makup to Morgan Lake	18	938 (14870)	639 (10130)	778 (12330)	485 (7690)	--	--	--	934 (14810)	1343 (21290)	1578 (25010)	1080 (17120)	890 (14110)	717 (11370)
Bottom Ash Sluice to Ash Pond	19	25.0 (396)	0 (0)	0 (0)	21.4 (339)	31.4 (498)	0 (0)	0 (0)	0 (0)	75.0 (1189)	68.5 (1086)	0 (0)	32.9 (521)	69.6 (1103)

*Flows are reported in ℓ/sec with GPM in parentheses.

TABLE 2-2. PARAMETERS CALCULATED BY THE EQUILIBRIUM PROGRAM FOR FOUR CORNERS SAMPLES*

Stream Name	Relative Saturations**			Equilibrium Partial Pressure of CO_2 atm	% Residual Electroneutrality
	$CaCO_3$	$Mg(OH)_2$	$CaSO_4 \cdot 2H_2O$		
Makeup Water	1.21	2.2×10^{-5}	0.21	4.8×10^{-4}	8.0
Scrubber Liquor (1A)	7.6×10^{-9}	5.3×10^{-15}	1.39	1.78×10^{-2}	-5.0
Scrubber Liquor (3A)	1.8×10^{-8}	1.5×10^{-14}	1.27	1.51×10^{-2}	-22.0
Thickener Overflow	3.8×10^{-7}	5.9×10^{-13}	1.28	9.55×10^{-3}	-5.0
Thickener Underflow	3.18	8.8×10^{-5}	0.50	2.3×10^{-4}	11.0
Bottom Ash Sluice	0.11	3.4×10^{-7}	0.19	6.96×10^{-3}	2.0
Sluice Tank Effluent	0.05	1.2×10^{-7}	1.19	2.57×10^{-3}	5.0
Ash Pond Effluent	7.10	6.9×10^{-4}	1.18	1.6×10^{-5}	-6.0
Ash Pond Surface	6.37	1.1×10^{-3}	1.11	2.3×10^{-5}	4.0

* These values were calculated using raw analytical data with all species concentrations and pH specified. The percent residual electroneutrality is the difference between the positive ions and the negative ions divided by the total charge times 100. This value gives an indication of analytical error as well as indicating the possible existence of an unaccounted for species in solution.

**Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$, about 2.5 for $CaCO_3$, and about 3.4 for $Mg(OH)_2$ (see Appendix C).

carbon dioxide because of the large amount of CO_2 in the flue gas. The carbonate level in the ash pond is depressed from the atmospheric value because $CaCO_3$ precipitation is occurring as indicated by the high relative saturations of $CaCO_3$.

The percent residual electroneutrality is the difference between the total positive charge and the total negative charge as a percent of the total charge. It is an indication of how accurately the actual stream is represented by the computer model. More information on the residual electroneutrality is presented in Appendix E. The values reported in Table 2-2 are quite good for the most part and tend to confirm the accuracy of the analysis.

2.1.1 Cooling and Bottom Ash Sluicing Systems

Water from Morgan Lake is used for both cooling and bottom ash sluicing. Water is brought into Morgan Lake from the San Juan River at a point 15 miles west of Farmington, New Mexico. This intake includes coarse trash racks, closure gates, traveling bar racks, sand traps and pumps. When the Four Corners plant was built, a permit to withdraw water from the San Juan River was obtained. However, this water could only be diverted at certain times of the year so Morgan Lake was constructed as a reservoir from which water could be continuously withdrawn for circulating water makeup, boiler water makeup, service water, cooling water, and ash sluicing water. Thus, Morgan Lake serves two purposes at the plant:

1) makeup water reservoir

2) cooling pond.

Morgan Lake has a surface area of about 5.16 km^2 (1,275 acres) with an average depth of 8.8 m (25 ft), and is located three miles south of the San Juan River. The circulating cooling water is withdrawn from the lake at the west end (deepest end) on the south shore. The condenser discharge is sent 1,520 m (5,000 ft) along the south shore through canals. Winds which are primarily from the southwest carry the warm water across the lake away from the plant intake (DE-165).

2.1.2 Particulate Scrubbing System

The potential for reduction of water requirements appears to be greatest in the wet scrubbing system. For this reason, the wet scrubbing system will be described in more detail than the cooling and ash sluicing systems. The particulate scrubbing system at Four Corners consists of six venturi scrubbers (two each for Units 1, 2, and 3), two thickeners, two thickener transfer tanks for return of thickener overflow and a sluice tank for combining thickener underflows and the scrubbing loop bleed stream. The scrubbing system is designed to clean 2.18 x 10^6 m^3 @ STP/hr (1.28 x 10^6 scfm) of gas at base load. The design slurry flow through the six scrubbers is 2880 ℓ/sec (45,700 GPM), resulting in a liquid-to-gas ratio of about 4.8 ℓ/m^3 @ STP (35.7 gal/1000 scf).

The flue gas and liquor undergo intimate contact as they flow through the venturi throat. The particulate removal efficiency is in excess of 99%, giving a scrubber outlet grain loading of about 92 mg/m^3 @ STP (.04 gr/scf). About 30% of the 600 ppm SO_2 in the flue gas is also transferred to the liquid phase, over 98% of which is oxidized to form sulfate in the scrubbing liquor.

The gas-liquid stream leaving the venturi throat passes through a disengagement zone where the liquid is separated from the gas and falls into a reservoir at the bottom of the scrubber. The gas passes through a demister to minimize entrainment and then to the stack. The liquor collected in the reservoir is recycled for further gas-liquid contacting after a bleed stream is removed. The major portion of this bleed stream is routed to the thickener and the remainder is sent to the sluice tank to reslurry the thickener underflow. The solids concentration in the recycle slurry is generally controlled between 1-2% by this bleed stream. Thickener transfer tank clear liquor, a combination of thickener overflow and makeup water, replaces the slurry which is removed from the scrubber recycle loop.

The scrubbing system is piped so that the two scrubber trains from each unit are connected to separate thickeners. In this manner, the system does not rely completely on one thickener train, so that if one thickener develops operating problems, the units can still operate at half load. The thickener underflow solids concentration can vary between 10% and 60% solids but typically is on the lower end of this range. Lime is added in the center of the thickeners to maintain the bottoms stream pH at approximately eight. This stream is sluiced with the bleed stream from the scrubber recycle loop to produce a waste stream of about 8% solids which is pumped to the ash pond for disposal. As mentioned previously, the thickener overflow streams are pumped to the thickener transfer tanks where makeup water is added. The clear liquor from these tanks is pumped to the scrubber reservoir on demand.

Water requirements for this scrubbing system depend primarily on two factors:

1) the evaporation rate in the scrubbers
2) the amount of water associated with the solid waste stream

The scrubber evaporation rate is approximately 30 ℓ/sec (470 GPM) when all scrubbers are operating at full load. When the slurry discharge stream sent to the pond is 8% solids, the water associated with this stream is about 190 ℓ/sec (3,000 GPM). The total water makeup requirements for the scrubbing system for October 1975 were about 3.4×10^8 ℓ (9.0×10^7 gal). This total includes the ash pond overflow liquor which is routed to the Chaco River and evaporation from both the ash pond and the scrubbers.

2.2 Existing Operations

The most severe operating problems related to water usage and disposal exist in the scrubbing system. Some SO_2 removal is achieved in the particulate scrubbers and gypsum scaling conditions have been reported. Also, a substantial portion of the water usage at Four Corners is related to the wet scrubbing system.

The following section presents an analysis of the design scrubber operating conditions based on sample analyses and operating data for the Four Corners plant. First, the simulation basis is presented, including a brief model description and a discussion of the input data used to simulate design conditions at Four Corners. Then the results of the simulations are compared to the sample results.

2.2.1 Simulation Basis

A process simulation of the Four Corners scrubbing system operating at design conditions was performed to characterize the system and to determine if a potential for water recycle/reuse exists with the present configuration. This section first briefly discusses the model, followed by a description of the operating parameters used as inputs to the model. A detailed discussion of the process model is included in Appendix E.

The process simulation flow scheme shown in Figure 2-2 was used to model the scrubbing system at Four Corners. This model calculates all stream compositions and flow rates using precipitation rate kinetics for $CaSO_4 \cdot 2H_2O$ and $CaSO_3 \cdot \frac{1}{2}H_2O$ (see Appendix C), which are the solids formed in lime/limestone scrubbing systems, and various input parameters. These parameters characterize the operating conditions for a particular scrubbing system and include flue gas flow and composition, fly ash rate and composition, makeup water composition, lime addition rate, tank volumes, scrubber feed flow rate and percent suspended solids, percent oxidation in the system, and percent solids in the sludge.

As shown by the order of process calculations in Figure 2-2, once the inputs are initialized and the first approximation for the thickener overflow (Stream 15) is made, SYSTB4 computes the compositions and flow rates for stack gas and scrubber effluent streams. Then iterative calculations are performed in Boxes 8, 9, and 10, completing the convergence loop until the composition of the thickener overflow remains with the specified convergence criterion. Then the remaining calculations are performed in Boxes 11 through 17.

Several assumptions are inherent in performing this simulation with the model outlined above. These are enumerated below:

1) The stack gas is saturated with respect to water.

2) Equilibrium exists between CO_2 in the stack gas and liquor in the scrubber bottoms.

3) The scrubber bottoms and stack gas temperatures are the adiabatic saturation temperature of the flue gas.

4) The scrubber was modeled without allowing solids precipitation to occur. However, dissolution of $Mg(OH)_2$, $Ca(OH)_2$, and $CaSO_3 \cdot \frac{1}{2}H_2O$ solids entering the scrubber was allowed. This dissolution pertains to particulates

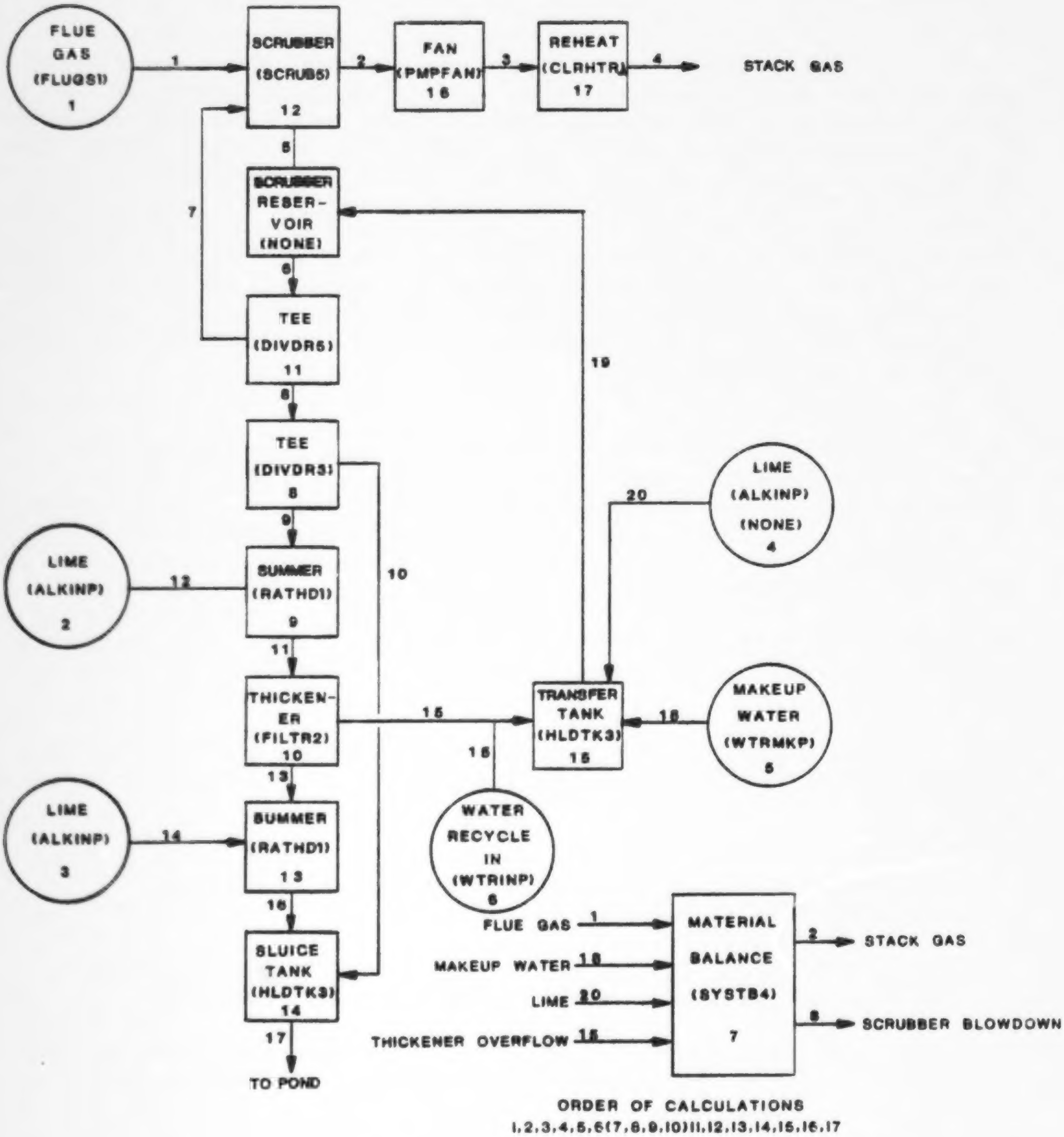

Figure 2-2. Four Corners scrubber simulation scheme (existing operations).

removed as well as slurry solids entering the scrubber. The fraction of each solid species that will dissolve in the scrubber was specified.

5) All oxidation was assumed to occur in the scrubber.

6) No $CaSO_4 \cdot 2H_2O$, $CaSO_3 \cdot \frac{1}{2}H_2O$, or $CaCO_3$ solids formed in the scrubbing loop. This was done to model the scrubber blowdown stream as accurately as possible. Realistically, actual conditions are somewhere between no precipitation and solid-liquid equilibrium. The short residence time in the scrubbing loop and the low inventory of precipitating solid crystals indicate that the assumption of no solids formation in the loop is adequate.

7) All solids precipitation occurs in reaction vessels (Subroutines HLDTK3 or RATHD1).

8) Ionic reactions taking place in the liquid phase are rapid and thus at equilibrium.

A summary of the input stream data employed in this simulation is provided in Table 2-3. The flue gas composition was determined by a combustion calculation from a coal analysis supplied by APS. The fly ash composition was provided by APS. The lime and water makeup compositions were measured by chemical analyses and adjusted to minimize the residual electroneutrality (Appendix E).

The system and equipment parameters are also listed in Table 2-3. The SO_2 sorption efficiency, SO_2 oxidation, gas phase pressure drop, particulate removal efficiency, scrubber blowdown pH and solids concentration, were either supplied by APS or computed from data obtained from APS. The fractions of CaO and MgO from the fly ash which hydrate in the system were computed from the results of ash characterization studies performed in support of this project (FU-R-61). The amount of hydration was determined from the leaching measured at low pH since this most closely approximates the existing scrubber operation at Four Corners.

TABLE 2-3. INPUT DATA FOR FOUR CORNERS SCRUBBING SIMULATION*

Flue Gas	
Flow, m^3/hr	4.1×10^6
(ACFM)	(2.41×10^6)
Temperature, °C	129
(°F)	265
Composition, mole %	
SO_2	0.0643
CO_2	13.1
O_2	4.65
N_2	74.58
H_2O	7.62
Fly Ash Rate, kg/min	975
(lb/min)	(2144)
System Parameters	
SO_2 Removal Efficiency, %	30
Oxidation, %	98.6
Particulate Removal Efficiency, %	99.7
Liquid-to-Gas Ratio, ℓ/m^3 @ STP	4.8
(gal/1000 scf)	35.7
Scrubber Slurry Solids, wt %	2.0
Thickener Underflow, wt % solids	10.0
Sludge, wt % solids	50
Makeup Water Composition, mg/ℓ	
Calcium	160.3
Magnesium	40.1
Sodium	188.6
Chloride	134.7
Carbonates (as $CO_3^=$)	77.4
Sulfates (as $SO_4^=$)	682
Nitrates (as NO_3^-)	9.3

*All flows are for all six scrubber modules.

2.2.2 Simulation Results

This section describes the results from the simulation of design scrubber operations at Four Corners. As Table 2-3 shows, some differences between the simulation and the sample data are to be noted, but overall the two compare favorably.

Comparison of some sample data with simulated results indicates that parts of the system may not have been at steady state during sampling. For instance, the thickener underflow stream's measured $CaSO_4 \cdot 2H_2O$ relative saturation was 0.5. Since gypsum precipitation was noted in the thickener and to some extent in the scrubber, it is not likely that the relative saturation would be much less than one. A second indication of unsteady state operation is the low (2.2%) solids concentration in the sluice tank effluent. Since the thickener underflow (10% solids) was sluiced by the scrubber effluent (2.2% solids), a concentration of 8% solids was simulated. Some of these discrepancies may be due to nonhomogeneous sampling and/or analytical errors as well as unsteady-state operation.

An examination of the existing operations at low slurry solids concentration (Table 2-4) reveals potential chemical scaling conditions at several points in the scrubbing loop. A section describing causes of chemical scaling is presented in Section 3.0. For discussion purposes here, it is noted that streams with relative saturations above 1.3 for $CaSO_4 \cdot 2H_2O$ and 2.5 for $CaCO_3$ may exhibit scale formation. The simulated scrubber effluent, thickener overflow, and thickener underflow all show $CaSO_4 \cdot 2H_2O$ relative saturations in the scaling region. Operation under these conditions for extended periods may necessitate system shutdown for cleaning. No carbonate scaling problems are indicated.

One method of reducing the amount of water consumed by the scrubbing system at the Four Corners plant is increasing the solids concentration of the solid waste stream. Since less water exits the system, less water makeup is required. A simulation of system operation at 30% solids in the thickener underflow and approximately 17% solids in the sluice tank effluent was performed. The results of this simulation are presented in Table 2-5. From this table it can be seen that the scaling potential is somewhat higher in the scrubber than at lower solids levels. It is obvious that the solution to the water recycle/reuse problems cannot be achieved simply by raising the solids content of the solid waste stream. Possible

TABLE 2-4. FOUR CORNERS SCRUBBING SIMULATION RESULTS FOR DESIGN CONDITIONS

Stream	Scrubber Liquor Blowdown*		Thickener Overflow		Thickener Underflow		Sluice Tank Effluent	
	Sample	Calculated	Sample	Calculated	Sample	Calculated	Sample	Calculated
Flow Rate,** ℓ/sec	800	785	750	590	10	140	120	190
(GPM)	(12,680)	(12,440)	(11,890)	(9,350)	(160)	(2,220)	(1,900)	(3,010)
pH	2.8	2.97	3.8	3.95	8.3	7.7	6.7	6.85
Suspended Solids, wt. %	2.8	2.0	.06	0	10.0	10.0	2.2	8.0
Relative Saturations ***								
$CaSO_4 \cdot 2H_2O$	1.39	1.38	1.28	1.30	0.50	1.31	1.19	1.0
$CaCO_3$	7.6×10^{-9}	1.3×10^{-7}	3.8×10^{-7}	1.1×10^{-5}	1.31	3.18	.05	1.0
Composition, mg/ℓ								
Calcium	794	854	734	802	333	822	702	662
Magnesium	48	55	53	55	38	55	46	55
Sodium	299	248	329	248	285	248	299	248
Chloride	163	160	178	160	107	160	156	160
Total Sulfur (as $SO_4^=$)	2,746	2,707	2,534	2,467	1,162	2,467	2,112	2,035
Sulfite (as $SO_3^=$)	8.0	31.2	17.6	31.2	--	27.2	--	25.6
Carbonate (as $CO_3^=$)	29	112	16	112	60	17	21	107
Nitrate (as NO_3^-)	25	11	24	11	7.4	11	20	11

*Blowdown at 2% solids (Scrubber 1A).

**Flow Rates under the Sample column are design flows. Simulations were performed with 10% solids in the thickener underflow rather than the design value of 60% because 10% is closer to actual operating practice.

***Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C).

TABLE 2-5. FOUR CORNERS SCRUBBING SIMULATION RESULTS WITH 30% SOLID WASTE OPERATION

Stream	Scrubber Liquor Blowdown	Thickener Overflow	Thickener Underflow	Sluice Tank Effluent
Flow Rate, ℓ/sec	160	81.5	26	79.7
(GPM)	(2,540)	(1,290)	(410)	(1,260)
pH	2.3	3.8	7.1	2.5
Suspended Solids, wt. %	9.0	0	30.0	17.3
Relative Saturations*				
$CaSO_4 \cdot 2H_2O$	2.52	1.30	1.32	1.0
$CaCO_3$	1.2×10^{-8}	7.7×10^{-6}	2.22	1.3×10^{-8}
Composition, mg/ℓ				
Calcium	1,480	794	846	642
Magnesium	77	77	77	77
Sodium	322	322	322	322
Chloride	188	188	188	188
Total Sulfur (as $SO_4^=$)	4,954	2,678	2,664	2,688
Sulfite (as $SO_3^=$)	72	72	72	72
Carbonate (as $CO_3^=$)	126	126	114	126
Nitrate (as NO_3^-)	12.4	12.4	12.4	12.4

* Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C).

alternatives for decreasing water use levels are presented in Section 3.0. Any attempt at decreasing the water makeup requirements to the scrubbing system must be accompanied by an effort to reduce the scaling potential which results.

3.0 TECHNICAL ALTERNATIVES

A key to reducing the water requirements for the particulate scrubbing system at the Four Corners Plant is producing a concentrated solid waste stream. An increase in solids concentration from 8% (existing operations) to 30% in the ash pond feed stream will reduce water requirements roughly by a factor of three. However, as was indicated in the plant characterization section, a scaling problem already complicates scrubber system operation. Further reduction of water makeup into the system which would result by increased waste solids concentration will compound these existing problems.

The Four Corners scrubbing system was originally designed for particulate scrubbing only, and several aspects of this system contribute to the scaling conditions which are currently in evidence. These aspects were considered in deciding upon practicable technical alternatives. The alternatives investigated include: (1) employing existing thickener transfer tanks as solid-liquid reaction vessels, (2) substantially increasing reaction tank capacity with two different liquid-to-gas ratios, (3) recycling ash pond overflow back to the scrubbing system utilizing two different hold-tank volumes, and (4) reducing the flue gas fly ash content into the scrubbers.

All alternatives considered in this study were simulated with an additional change from existing operating procedure. The recirculating slurry was specified to be 10 weight percent solids rather than 2 percent. This increase in solids concentration will tend to lower the relative saturation required for a specified set of system operating parameters. This will also assist with the elimination of chemical scaling conditions.

The reasons for considering each alternative are explained in this section. Flowsheets are provided in order to point out the differences between the models used for the alternative simulations and the one used for existing operations. The results from each simulation are discussed from a standpoint of technical feasibility. Finally, conclusions drawn from these simulations are presented in the last subsection.

3.1 Alternative One

One major problem with the Four Corners scrubbing system is lack of reaction time (hold tank volume) for solid-liquid mass transfer. Alternative 1 proposes a means of doubling the solid-liquid reaction time by utilizing existing tank capacity available in the present system. In this section the simulation basis for this alternative is presented followed by the results of the simulation.

3.1.1 Simulation Basis

The present system configuration (Figure 2-1) provides only minimal solid-liquid contact (approximately one minute) in the scrubber recirculation loop. This holding time is insufficient as evidenced by the present scaling conditions. If the solid concentration in the solid waste stream is increased and the water make-up requirements reduced, these scaling problems will worsen.

One method of providing additional reaction time would be to use the existing thickener transfer tanks as solid-liquid reaction tanks. This was the first alternative considered. A schematic flow diagram of Alternative 1 is shown in Figure 3-1. (The same flow scheme would be used for the 'B' scrubber train but is not pictured.) The system modifications required to implement this alternative are largely piping changes.

The major system alteration is that the slurry recirculation loop has been changed to encompass the transfer tank and the scrubber reservoir rather than only the scrubber reservoir. In the existing operational flow scheme, the transfer tank contains only clear liquor from the thickener overflow and precipitation takes place only by nucleation. With Alternative 1, approximately one minute of additional solid-liquid reaction time is provided.

A small tank contained within the transfer tank has also been proposed. An opening in the small tank at the base would allow liquor to flow through the small tank to the transfer tank. All streams enter the transfer tank through the proposed new tank. The function of this tank would be primarily one of mixing the scrubber effluent stream with the lime slurry additive. This would produce high relative saturations resulting in controlled nucleation in this tank. It was reasoned that by providing a small volume tank with high

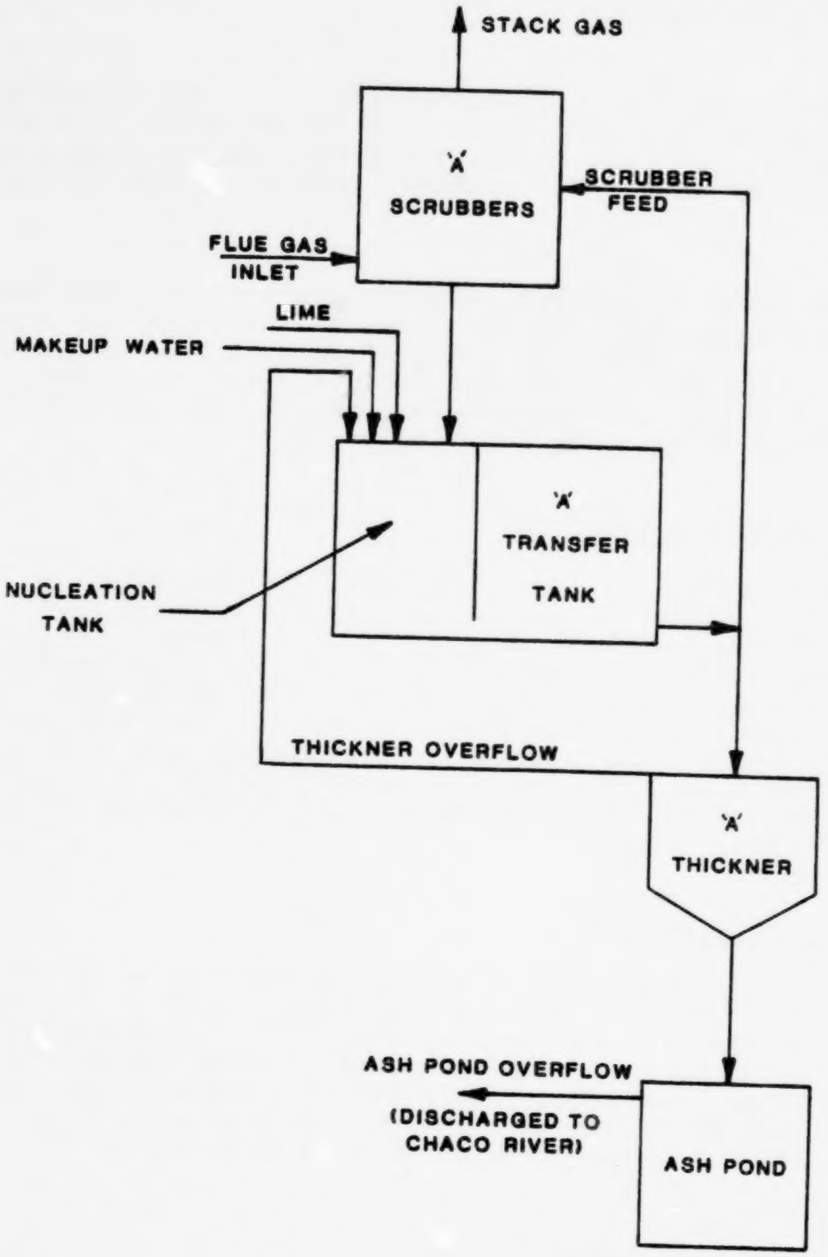

Figure 3-1. Schematic flow diagram for Four Corners Alternative One.

precipitation driving forces sufficient nucleation and precipitation rates might occur in the tanks such that scaling could be avoided in the scrubber.

Employing this system configuration, the thickener feed stream would be a slipstream from the transfer tank effluent (scrubber feed). As such, no lime addition to the thickener would be required since the thickener feed pH should be between 6 and 8.

In order to simulate Alternative 1 a new model was made of the scrubbing system. A flow sheet of this model is presented in Figure 3-2. This model is somewhat simpler than the model used for existing operations, but is sufficient to illustrate the effect that a larger hold tank volume has on the $CaSO_4 \cdot 2H_2O$ scale potential in the scrubbing loop.

3.1.2 Simulation Results

The results of this simulation are presented in Table 3-1. The key to these results is the relative saturation of $CaSO_4 \cdot 2H_2O$ in the scrubber effluent. The value of 1.33 indicates that scrubber operation under these conditions would be at the risk of gypsum scale formation. It should be noted here that calcium carbonate and gypsum precipitation is over 90% nucleation in this system configuration. Considering the results of this simulation case, it does not appear that this nucleation can be controlled and this alternative was judged not to be technically feasible.

3.2 Alternative Two

Since elimination of scaling potential in the scrubber could not be achieved by implementing Alternative 1, increasing reaction tank capacity further was the next alternative considered. For Alternative 2 to become an operational system, tanks would have to be installed. Two separate liquid-to-gas ratios were considered with this alternative. This section presents the simulation basis and the results of the simulation of Alternative 2.

3.2.1 Simulation Basis

Implementation of Alternative 2 would provide 37,500 m^3 (1.33×10^6 ft^3) of combined reaction volume for the entire scrubbing system. A process flow diagram for this alternative is shown in Figure 3-3.

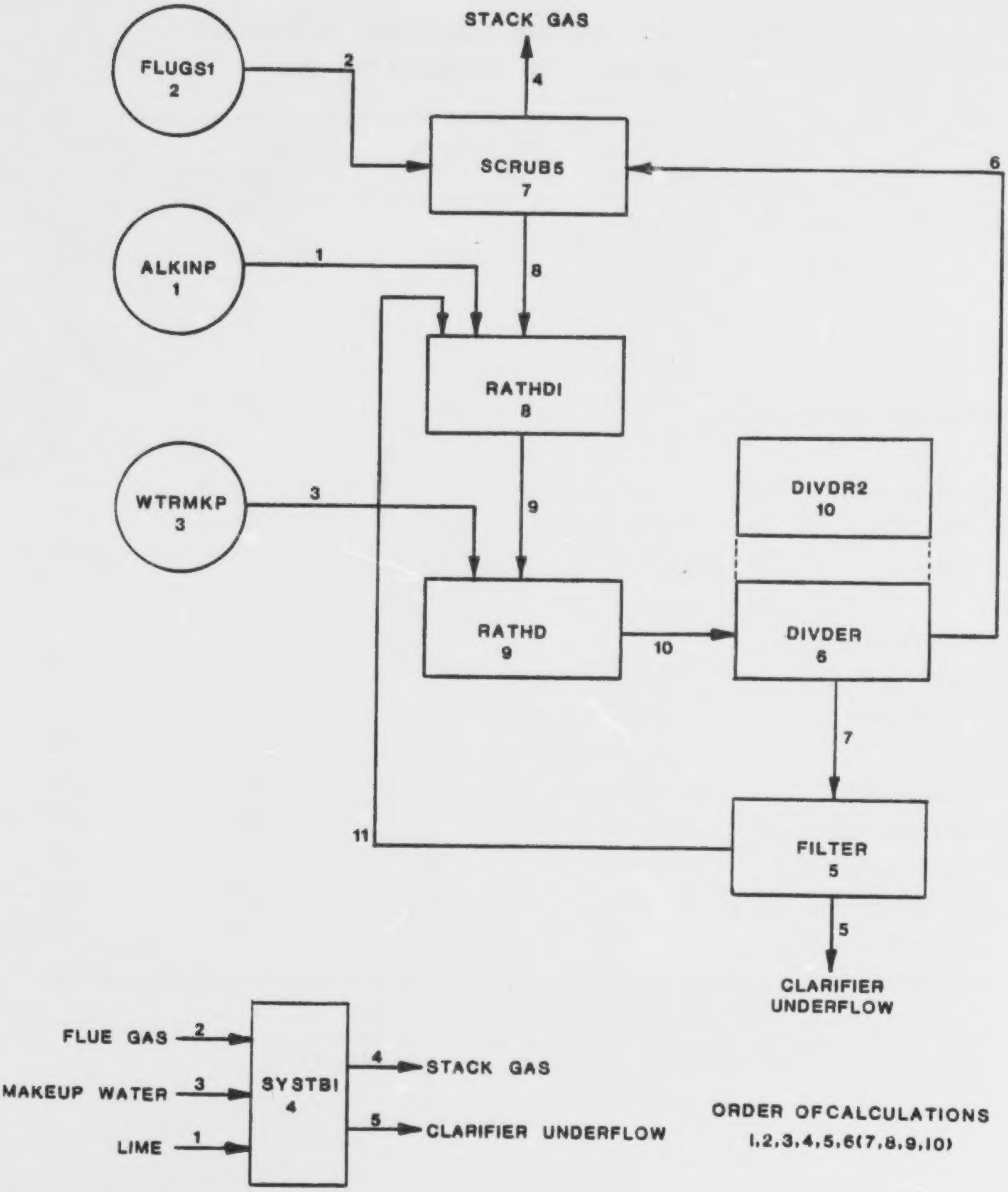

Figure 3-2. Process model for Four Corners Alternative One.

TABLE 3-1. FOUR CORNERS SCRUBBING SIMULATION RESULTS FOR ALTERNATIVE ONE *

Stream	Scrubber Effluent	Nucleation Tank Effluent	Transfer Tank Effluent	Filter Bottoms
Flow Rate, ℓ/sec	160	2,840	2,960	42
(GPM)	(2,550)	(45,000)	(46,900)	(670)
pH	2.8	7.2	7.1	6.9
Suspended Solids, wt %	10	10	10	30
Relative Saturations**				
$CaSO_4 \cdot 2H_2O$	1.33	1.3	1.26	1.0
$CaCO_3$	4.8×10^{-8}	3.5	2.3	1.0
Composition, mg/ℓ				
Calcium	793	802	816	630
Magnesium	82	83	83	82
Sodium	442	447	449	442
Chloride	233	236	236	233
Sulfate (as $SO_4^=$)	2,659	3,042	2,722	2,330
Sulfite (as $SO_3^=$)	72	76	74	28
Carbonate (as $CO_3^=$)	116	121	120	111
Nitrate (as NO_3^-)	16	16	16	16

* Makeup water flow rate is 71.5 ℓ/sec (1,130 GPM).

** Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$, and about 2.5 for $CaCO_3$ (see Appendix C).

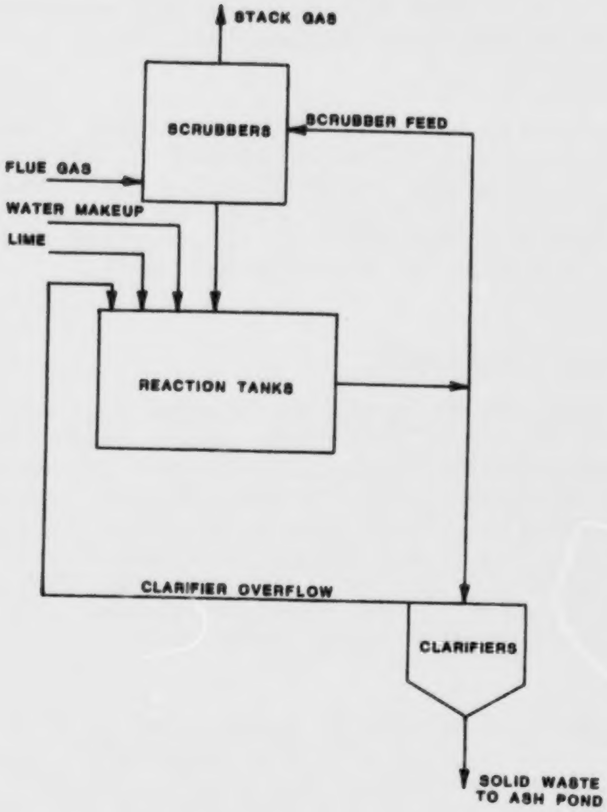

Figure 3-3. Process flow diagram for Four Corners Alternative Two.

Basically, the philosophy represented by this alternative is one of allowing sufficient solid-liquid reaction time so that nucleation does not occur anywhere within the system. This can be done by providing sufficient reaction tank volume and supplying the scrubber feed slurry from the reaction tank effluent. Also, two different L/G's were simulated. The first was the present design L/G of 4.7 ℓ/m^3 @ STP (35.2 gal/1000scf). The second L/G which was simulated was approximately 10 ℓ/m^3 @ STP (74.8 gal/1000 scf). The second case was performed because the simulated scrubber effluent pH was low, about 2.9.

The process model used to simulate Alternative 2 is presented in Figure 3-4. The principal differences between the simulation of Alternative 1 and Alternative 2 are (1) the reaction tank volume is much larger in Alternative 2 and (2) only one reaction tank is simulated in Alternative 2 instead of two smaller tanks in series as in Alternative 1.

3.2.2 Simulation Results

The results from the two cases considered in Alternative 2 are presented in Table 3-2. Both cases model a system which could effectively remove 50% of the SO_2 from the flue gas without gypsum scaling. The gypsum relative saturations for the scrubber effluent liquor are 1.16 and 1.14 for Cases 1 and 2, respectively. These are well below the level required for the onset of scaling. In fact, these cases represent systems with very conservative sized reaction tanks. Hold tank sizing will be addressed in subsequent sections.

A simulated scrubber bottoms pH of 2.9 resulted when the design L/G, 4.7 ℓ/m^3 @ STP (35.2 gal/1000 scf) was employed. This pH could cause corrosion and possibly other operating problems if the system operated in this manner for extended periods of time. With this in mind, the system was simulated using an L/G of 10.0 ℓ/m^3 @ STP (74.8 gal/1000 scf). An increase in L/G will cause a smaller pH drop across the scrubber since less SO_2 is absorbed per liter of liquor. Since the increase in acidic species concentration across the scrubber is smaller with the higher L/G, the scrubber bottoms pH should rise.

A scrubber bottom pH of 3.9 was calculated for this case. This operating condition is still not ideal from the standpoint of corrosion control; however, it is somewhat better than 2.9 pH scrubber liquor. The proposed L/G is certainly within the normal operating range for most venturi scrubbers.

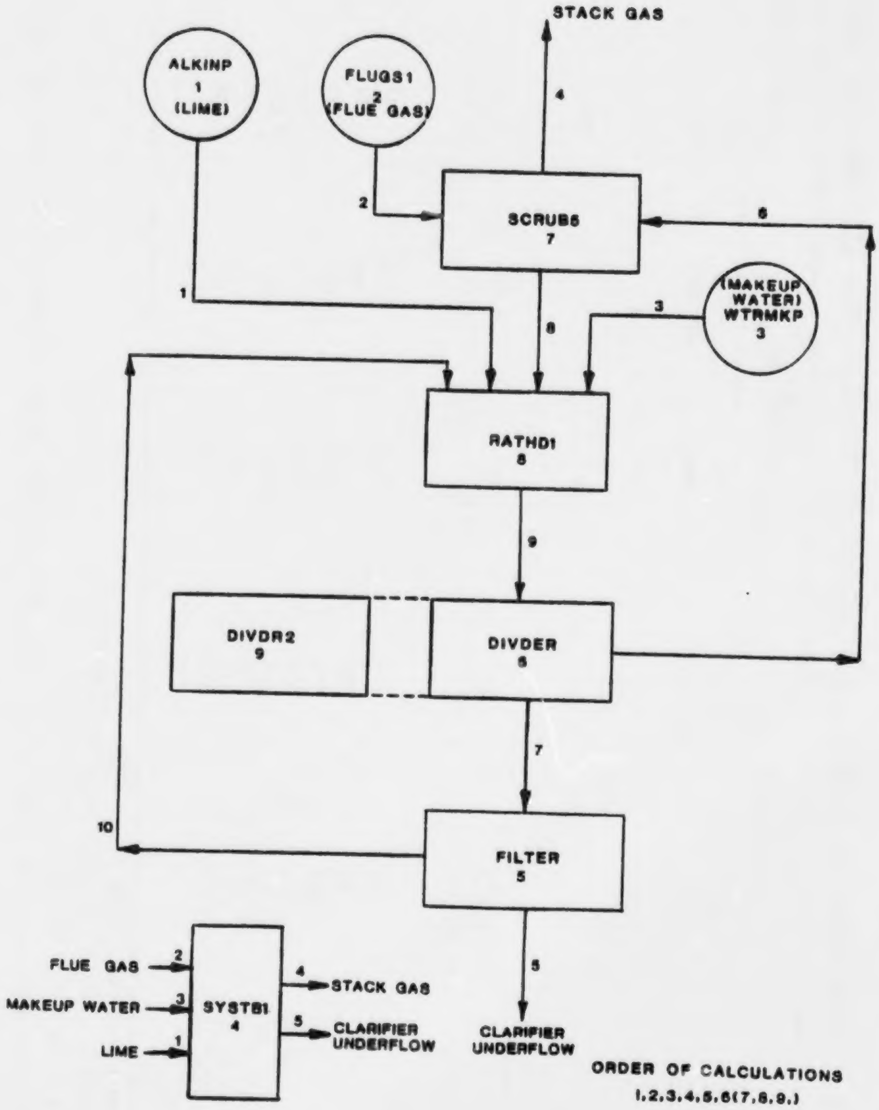

Figure 3-4. Process model for Four Corners Alternative Two.

TABLE 3-2. FOUR CORNERS SCRUBBING SIMULATION RESULTS FOR ALTERNATIVE TWO*

Stream	Scrubber Effluent		Reaction Tank Effluent		Filter Bottoms	
	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2
Flow Rate, ℓ/sec	2827	6048	3,016	6,235	40.9	40.9
(GPM)	(44,800)	(95,800)	(47,800)	(98,800)	(650)	(650)
pH	2.9	3.9	6.9	6.9	6.9	6.9
Suspended Solids	10	10	10	10	30	30
Relative Saturations**						
$CaSO_4 \cdot 2H_2O$	1.16	1.14	1.07	1.07	1.0	1.0
$CaCO_3$	1.0×10^{-7}	6.7×10^{-6}	1.03	1.03	1.0	1.0
Composition, mg/ℓ						
Calcium	674	673	674	673	631	631
Magnesium	84	84	84	84	84	84
Sodium	447	446	447	446	447	447
Chloride	235	235	235	235	235	235
Sulfate (as $SO_4^=$)	2,432	2,431	2,432	2,431	2,336	2,336
Sulfite (as $SO_3^=$)	34	33	34	33	28	28
Carbonate (as $CO_3^=$)	116	116	116	116	116	116
Nitrate (as NO_3^-)	15	16	16	16	16	16

*Makeup water flow rate is 70.7 ℓ/sec (1,120 GPM)
Case 1 has a L/G of 4.7 ℓ/m^3 @ STP (35.2 gal/1,000 scf)
Case 2 has a L/g of 10 ℓ/m^3 @ STP (74.8 gal/1,000 scf)

**Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$, and about 2.5 for $CaCO_3$ (see Appendix C).

It is noted that the higher L/G does reduce further the gypsum relative saturation in the scrubber effluent stream. For these reasons, the remaining simulations were conducted using the 10.0 ℓ/m^3 @ STP liquid-to-gas ratio. Operation of the Four Corners scrubbing system at this L/G probably will require increased pumping capacity.

3.3 Alternative Three

Further reduction of water requirements could be achieved by recycling the ash pond overflow which is currently discharged into the Chaco River. This is desirable from a water use standpoint as well as from an emissions viewpoint. Simulation of this alternative assists in evaluating the impact of this recycle on the scrubbing system. This section presents the simulation basis and the results of the simulation of Alternative 3.

3.3.1 Simulation Basis

Figure 3-5 indicates the flow scheme for this alternative. This is the same system as was modeled in Alternative 2 with the exception that the ash pond overflow is returned to the scrubbing system reaction tank. This water has a much higher total dissolved solids level than does the makeup water taken from Morgan Lake. The objective of simulating this alternative was to measure the impact that the poorer quality water might have on the operation of the scrubber system.

Two cases were considered in this alternative. The first case simulated the system with a 37,500 m^3 (1.33 x 10^6 ft) reaction tank. This is the same volume tank which was modeled in Alternative 2. The second case simulated a system with perhaps a more realistically sized reaction tank (21,200 m^3 or 7.5 x 10^5 ft^3). The process model used to simulate this alternative is presented in Figure 3-6.

3.3.2 Simulation Results

The results from Alternative 3 are summarized in Table 3-3. The recycle of ash pond overflow to the scrubbing system has no major impact on the simulated scrubber bottoms gypsum relative saturation. The water requirements would be reduced by 19.9 ℓ/sec (315 gpm) with this system configuration.

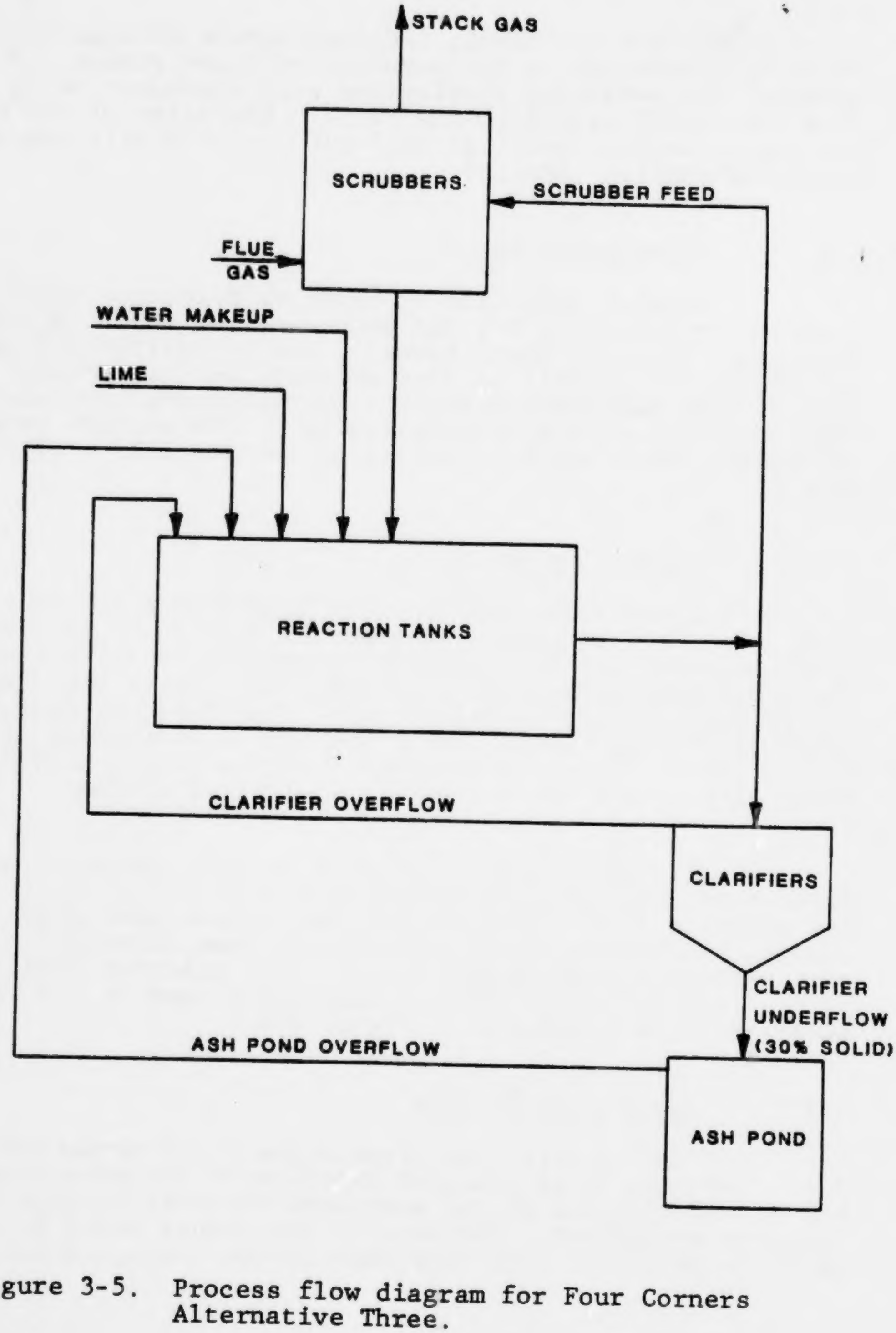

Figure 3-5. Process flow diagram for Four Corners Alternative Three.

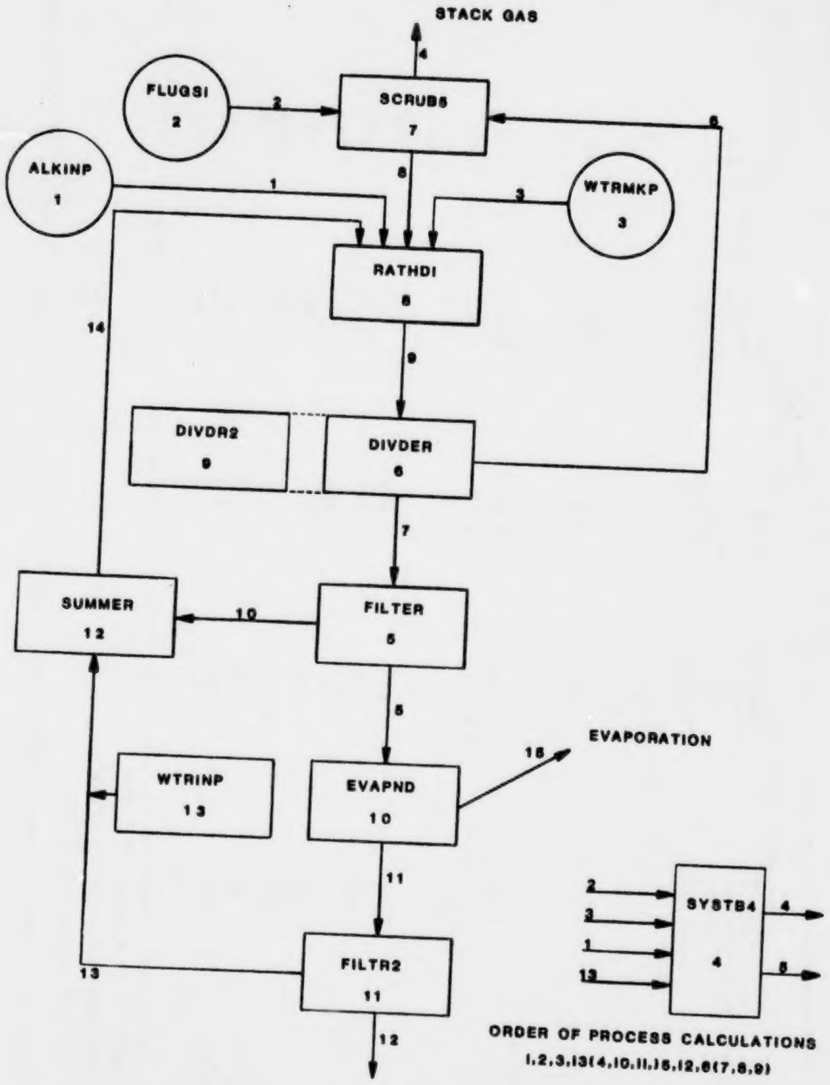

Figure 3-6. Process model for Four Corners Alternative Three.

TABLE 3-3. FOUR CORNERS SCRUBBING SIMULATION RESULTS FOR ALTERNATIVE THREE*

Stream	Scrubber Effluent		Reaction Tank Effluent		Filter Bottoms	
	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2
Flow Rate, ℓ/sec	6048	6048	6,230	6,230	40.8	40.8
(GPM)	(95,800)	(95,800)	(98,700)	(98,700)	(650)	(650)
pH	3.8	3.7	7.0	7.0	7.0	7.0
Suspended Solids, Wt. %	10	10	10	10	30	30
Relative Saturations **						
$CaSO_4 \cdot 2H_2O$	1.14	1.19	1.04	1.12	1.0	1.0
$CaCO_3$	4.5×10^{-6}	2.7×10^{-6}	1.03	1.05	1.0	1.0
Composition, mg/ℓ						
Calcium	641	673	641	673	599	599
Magnesium	145	138	145	138	145	138
Sodium	793	757	793	757	793	757
Chloride	386	361	386	361	386	361
Sulfate (as $SO_4^=$)	3,017	3,118	3,107	3,118	3,014	2,952
Sulfite (as $SO_3^=$)	35	40	35	40	30	29
Carbonate (as $CO_3^=$)	105	93	105	93	105	93
Nitrate (as NO_3^-)	25	23	25	23	25	23

*Makeup water flow rate is 50.8 ℓ/sec (805 GPM)
Case 1 has a reaction tank volume of 37,500 m^3
Case 2 has a reaction tank volume of 21,200 m^3

**Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C).

Case 2 represents a reduction in reaction tank capacity from 37,500 m^3 (1.33 x 10^6 ft^3) to 21,200 m^3 (7.5 x 10^5 ft^3). The gypsum relative saturation in the scrubber effluent increased from 1.14 to 1.19. A well designed and well controlled system can function adequately at gypsum relative saturations up to 1.25 in the scrubber slurry stream. Above this control point fluctuations in the operation of a system would make scale control in the scrubber difficult.

Case 2 represents a realistically sized reaction tank based on the information available. Further size reduction simulations were not considered to be cost effective for several reasons. Proper design of a scrubbing system would require further testing and data gathering to be performed.

3.4 Alternative Four

One final alternative, a system design where a 60% efficient particulate control device (such as a mechanical collector) is placed upstream of the scrubbing system, was considered. The discussion of this alternative will be brief since very few changes from Alternative 3 were necessary to model Alternative 4.

3.4.1 Simulation Basis

Figure 3-7 is a process flow diagram for Alternative 4. A 60% efficient mechanical collector has been located prior to the venturi scrubbers. Otherwise this diagram is identical to the flow sheet presented for Alternative 3. Therefore, the process model used for Alternative 4 is the same as that used for Alternative 3. The difference between these two alternatives is the fly ash concentration of flue gas which enters the scrubber. In Alternative 4, this concentration is only 40% of that specified for Alternative 3. This, in effect, simulates a 60% efficient mechanical collector. From the standpoint of water recycle/reuse, it is assumed that the fly ash removed by the mechanical collector would be disposed of by dry methods. With less fly ash solids being removed, the reaction tank volume required to maintain non-scaling conditions is reduced. Since more of the recirculated solids will be gypsum, more sites are provided for precipitation, which reduces the reaction time required for gypsum formation.

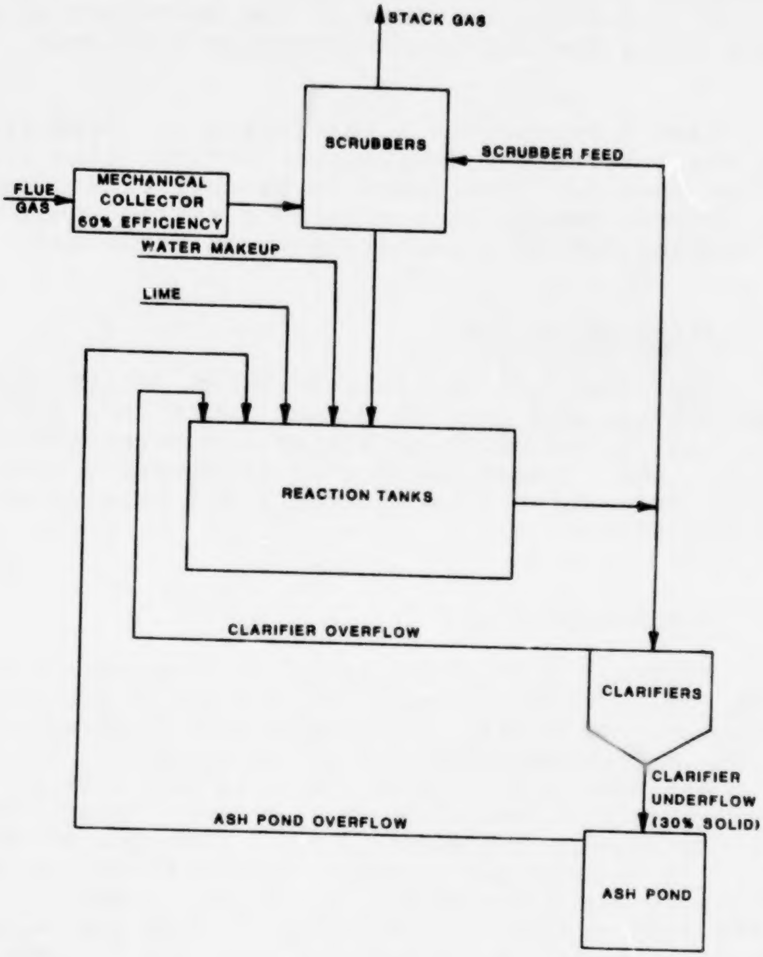

Figure 3-7. Process flow diagram for Four Corners Alternative Four.

TABLE 3-4. FOUR CORNERS SCRUBBING SIMULATION RESULTS FOR ALTERNATIVE FOUR*

Stream	Scrubber Effluent	Reaction Tank Effluent	Filter Bottoms
Flow Rate, ℓ/sec	6,039	6,142	18.7
(GPM)	(95,700)	(97,300)	(296)
pH	3.6	7.0	7.0
Suspended Solids	10.1	10	30
Relative Saturations**			
$CaSO_4 \cdot 2H_2O$	1.19	1.14	1.0
$CaCO_3$	2.0×10^{-6}	1.05	1.0
Composition, mg/ℓ			
Calcium	692	685	604
Magnesium	157	156	156
Sodium	825	821	822
Chloride	447	445	445
Sulfate (as $SO_4^=$)	3,377	3,225	3,044
Sulfite (as $SO_3^=$)	44	42	30
Carbonate (as $CO_3^=$)	108	106	107
Nitrate (as NO_3^-)	29	29	29

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* Makeup water flow rate is 41 ℓ/sec (650 GPM).

**Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C).

3.4.2 Simulation Results

Table 3-4 presents a summary of the Alternative 4 results. Two results of a special note should be mentioned here. First, the reaction tank volume required to achieve non-scaling conditions is less than that needed in any of the other technically feasible alternatives considered in this study. This volume for Alternative 4 is 8,900 m^3 (3.14×10^5 ft^3) compared to 21,200 m^3 (7.5×10^5 ft^3) for Case 2 of Alternative 3. This reduction is directly attributable to the reduction in the fly ash removal by the scrubbing system. Less of the circulated solids are inert fly ash and more of the solids are gypsum. The increase in precipitation sites lowers the reaction time required for gypsum precipitation.

A second result which is also a consequence of removing a portion of the fly ash prior to the scrubbing system is the reduction in water makeup requirements. A 20% decrease (from Case 2 of Alternative 3) in the water makeup flow is noted. Again, this result is based on the assumption that dry methods would be employed in the disposal of the fly ash removed.

It should also be mentioned that lime requirements are increased in this alternative. Since less fly ash is picked up by the scrubbing system, less alkalinity is derived from the sorbed fly ash. The increase in lime flow was from 30 to 40 kg/min.

3.5 Conclusions

This section discusses the conclusions which can be drawn from the simulation of the various alternatives. A summary of the simulation results is provided in Table 3-5. The conclusions are listed below:

1) Alternatives 2, 3 and 4 are technically feasible from the standpoint of scale control. It appears that present system tankage capacity (Alternative 1) is not sufficient to achieve scale-free operation.

2) Based on data available, it is difficult to model the Four Corners System from the standpoint of accurately predicting SO_2 removal and sulfite oxidation. Further testing is recommended before detailed

TABLE 3-5. FOUR CORNERS WATER MANAGEMENT SIMULATIONS SUMMARY

	Existing Operations		Alternative 1	Alternative 2		Alternative 3		Alternative 4
	Case 1	Case 2	Case 1	Case 1	Case 2	Case 1	Case 2	Case 1
Hold Tank Volume, m^3	--	--	214*	37,500	37,500	37,500	21,200	8,900
L/G, ℓ/m^3 @ STP	4.7	4.7	4.7	4.7	10.0	10.0	10.0	10.0
Scrubber Bottoms								
pH	2.6	2.3	2.8	2.9	3.9	3.8	3.7	3.6
$CaSO_4 \cdot H_2O$ R.S. **	1.38	2.52	1.33	1.16	1.14	1.14	1.19	1.19
Thickener Bottoms								
% Solids	10.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0
pH	7.7	7.1	6.9	6.9	6.9	7.0	7.0	7.0
Water Makeup Requirements, ℓ/sec	223	109	71.5	70.7	70.7	50.8	50.8	41.0

*Combined volume of proposed nucleated hold tank and existing transfer tank.

**Based on 98.6% oxidation.

Comments:

Alternative 1: This alternative would utilize existing thickener transfer tanks as reaction tanks. Small nucleating tanks within these transfer tanks were also modeled. The resulting scrubber effluent gypsum relative saturation would cause continued scaling problems in the scrubber.

Alternative 2: To reduce the scaling potential in the scrubber, a much larger reaction tank was specified in Alternative 2. This lowered the gypsum relative saturation. However, a 2.9 pH may cause additional operating problems so that L/G was increased. This resulted in a more reasonable pH.

Alternative 3: Alternative 3 involves modeling recycle of ash pond overflow to reduce water makeup requirements. Case 2 represents a more realistically sized hold tank. A gypsum relative saturation between 1.2 and 1.25 in the scrubber bottoms stream is generally acceptable for nonscaling scrubber operation.

Alternative 4: Alternative 4 models a system which has a 60% efficient particulate collection device prior to the wet scrubbing system. A marked decrease in required hold tank volume is noted. Water makeup requirements would also be reduced if the fly ash was disposed of by dry methods.

hold tank sizing and any scrubbing system alterations are attempted. It is felt that the 50% SO_2 removal and 98% oxidation levels which were specified are adequate to indicate trends and evaluate alternatives. This 50% SO_2 removal corresponds to roughly 0.7 pounds of emitted SO_2 per million Btu which is well below the existing Federal new source standard of 1.2 lb SO_2/MM Btu.

3) A large increase in reaction tank volume will be necessary to eliminate scaling problems in the scrubber with the existing oxidation level. More detailed information on SO_2 removal rate, venturi contactor efficiency, effect of fly ash erosion of scale, and effects of process modifications on oxidation is essential in correctly sizing these tanks.

4) The present pump capacity may produce a scrubber effluent slurry which could cause operating problems due to low pH. Doubling the pump capacity (increasing the liquid-to-gas ratio from 4.7 to 10 ℓ/m^3 @ STP or from 35.2 to 74.8 gal/1000 scf) will increase the scrubber bottoms pH and tend to lessen the scaling tendency of this stream.

5) Recycle of ash pond overflow has little impact on the operation of the scrubbing system. Considerable reduction of water makeup requirements would be achieved by implementing this alternative. A major reduction in makeup water requirements can be achieved simply by increasing the thickener underflow from 10% to 30% solids.

6) Separate equipment for fly ash removal could decrease water requirements and reduce the size of the reaction tanks required. Decreased fly ash in the system may reduce erosion and possibly alleviate other potential operating difficulties.

4.0 ECONOMICS

This section provides cost estimation for implementing each of the technically feasible alternatives discussed in Section 3.0. Both rough capital costs and operating costs are presented. The assumptions and techniques used in calculating these costs are briefly outlined. It should be emphasized here that these economics are only rough estimates for comparative purposes.

A capital cost summary for the technically feasible alternatives is provided in Table 4-1. All of these alternatives involve the addition of six reaction tanks, two agitators per tank to keep the slurries well mixed, and additional pumping capacity. Alternatives 3 and 4 require piping to recycle the ash pond water and Alternative 4 uses a cyclone for particulate removal before the scrubber. All values are in 1976 dollars.

The tank costs are given for field-erected tanks of carbon steel construction. These costs include the addition of a wear liner, mixer supports, baffles, nominal foundations and plumbing. Engineering and labor costs were estimated for each to be approximately 24% of the material costs (GU-075). Terrain and soil characteristics may require special site preparation which will add to installation costs and the costs for interconnecting plumbing and pumping will also be a function of the particular site. Agitator costs were determined for twelve 50 hp electrically driven agitators with rubber coated impellers.

The additional pumps used to increase the L/G were assumed to be 300 hp electrically driven centrifugal pumps. The pumps are rubber-lined and have wear-resistant impellers. Six pumps will be required with a capacity of about 8,500 GPM each. The pump used to transport the 650 GPM 30% solids slurry out to the ash pond will be a 25 hp reciprocal pump. To return 350 GPM of water from the ash pond, a 5 hp centrifugal pump will be employed. A labor to material ratio of 0.36 was used for installation costs and engineering was assumed to be 10% of the combined labor and material costs (GU-075).

The piping costs are for the half mile of pipe required to transport the 30% slurry out to the ash pond. Five inch carbon steel pipe with average fittings, flanges, shop coating, wrapping, and lined with rubber was assumed to extend the full distance. A labor to material cost ratio of 0.8 was used to determine the cost of underground installation.

TABLE 4-1. CAPITAL COSTS FOR WATER RECYCLE/REUSE ALTERNATIVES AT FOUR CORNERS*

Item	Alternative 2		Alternative 3		Alternative 4
	Case 1 (1976 dollars)	Case 2 (1976 dollars)	Case 1 (1976 dollars)	Case 2 (1976 dollars)	Case 1 (1976 dollars)
Hold Tanks	2,387,000	2,387,000	2,387,000	1,565,000	1,060,000
Agitators	312,000	312,000	312,000	312,000	312,000
Pumps and Drivers	12,000	777,000	777,000	777,000	777,000
Piping	---	---	43,000	43,000	43,000
Cyclone	---	---	---	---	560,000
Contingency (20%)	542,000	695,000	704,000	539,000	550,000
Contractural Fees (3%)	81,000	104,000	106,000	81,000	83,000
Total	3,334,000	4,275,000	4,328,000	3,317,000	3,385,000

*Based on 98.6% oxidation in the scrubbers.

Comments:

Alternative 2: To reduce the scaling potential in the scrubber, a much larger reaction tank was specified in Alternative 2. This lowered the gypsum relative saturation. However, a 2.9 pH may cause additional operating problems so that L/G was increased. This resulted in a more reasonable pH.

Alternative 3: Alternative 3 involves modeling recycle of ash pond overflow to reduce water makeup requirements. Case 2 represents a more realistically sized hold tank. A gypsum relative saturation between 1.2 and 1.25 in the scrubber bottoms stream is generally acceptable for nonscaling scrubber operation.

Alternative 4: Alternative 4 models a system which has a 60% efficient particulate collection device prior to the wet scrubbing system. A marked decrease in required hold tank volume is noted. Water makeup requirements would also be reduced if the fly ash was disposed of by dry methods.

Engineering costs (direct and indirect) were assumed to be 7.2% of the combined labor and material cost (GU-075).

Table 4-2 presents the operating costs associated with the different alternatives presented for Four Corners. These values are reported in 1976 dollars per year. Power costs were based on an 80% load factor and a wholesale price of 2¢/kw-hr for electricity. Capital cost amortization is also included using 15% per year for a 30 year lifetime.

A comparison of Alternative 3, case 2 with Alternative 4 shows that the reduction in capital cost due to a reduction in the required reaction volume when cyclones are employed is roughly offset by the cost of the cyclones. These costs are based on installation of new dust collectors. Existing collectors are presently inoperable on Units 1, 2, and 3 at Four Corners, but it may be possible to place these in working order at less expense than supplying new cyclones.

An alternate method of reducing the water makeup requirements from Morgan Lake would be to purify the ash pond overflow and return it to the system rather than routing the overflow to the Chaco River. (It is not possible to recycle the ash pond overflow with the existing system configuration because of scaling problems). However, this stream flow is about 173 liters/sec (2760 GPM). A brine concentrator/reverse osmosis unit designed to handle this flow would be about $8.5 million capital investment (RE-211). Furthermore, this method would not significantly improve the existing scaling problems.

It is emphasized here that these costs are based on a system which achieves 50% SO_2 removal. The reaction tanks were roughly sized accordingly. The economics and system design could change somewhat in the event that greater than 50% removal is feasible under the proposed venturi scrubber operating conditions. With this limitation in mind and without further testing, either Alternative 3, case 2 or Alternative 4 would be recommended. Ash pond overflow recycle appears to be feasible and the higher L/G is recommended. The size of the reaction tanks depends on whether dust collectors are employed upstream of wet scrubbers.

An additional 10 liters/sec (160 GPM) of water makeup can be eliminated by employing dust collectors. Implementation of Alternative 4 necessitates specific plant information such

TABLE 4-2. OPERATING COSTS FOR WATER RECYCLE/REUSE ALTERNATIVES AT FOUR CORNERS*

	Alternative 2		Alternative 3		Alternative 4
Item	Case 1 (1976 dollars)	Case 2 (1976 dollars)	Case 1 (1976 dollars)	Case 2 (1976 dollars)	Case 1 (1976 dollars)
Power for the Agitators	125,000	125,000	125,000	125,000	125,000
Power for the Pumps	3,000	335,000	335,000	335,000	335,000
Capital Charges (15% per year)	500,000	641,000	649,000	498,000	508,000
Total	628,000	1,101,000	1,109,000	958,000	968,000
(mils/kW-hr)**	(.128)	(.225)	(.226)	(.195)	(.198)

*Based on 80% load factor

**Power production from Units 1, 2, and 3 (700 MW)

Comments:

Alternative 2: To reduce the scaling potential in the scrubber, a much larger reaction tank was specified in Alternative 2. This lowered the gypsum relative saturation. However, a 2.9 pH may cause additional operating problems so the L/G was increased. This resulted in a more reasonable pH.

Alternative 3: Alternative 3 involves modeling recycle of ash pond overflow to reduce water makeup requirements. Case 2 represents a more realistically sized hold tank. A gypsum relative saturation between 1.2 and 1.25 in the scrubber bottoms stream is generally acceptable for nonscaling scrubber operation.

Alternative 4: Alternative 4 models a system which has a 60% efficient particulate collection device prior to the wet scrubbing system. A marked decrease in required hold tank volume is noted. Water makeup requirements would also be reduced if the fly ash was disposed of by dry methods.

as erosion problems caused by fly ash slurry and ease of dry disposal of the fly ash collected in the dust collection devices.

Appendix G. Recycle/Reuse Options at Bowen (Georgia Power Company)

1.0 INTRODUCTION

This appendix describes the analysis of the water system at the Georgia Power Company's (GPC) Plant Bowen under EPA Contract No. 68-03-2339, Water Recycle/Reuse Alternatives in Coal-Fired Steam-Electric Power Plants. This section presents a summary of the important results of the study concerning Bowen. Bowen was chosen with four other plants for evaluation of the technical and economic feasibility of various water recycle/reuse options. The major water systems at the four-unit, 3180 Mw Bowen Plant are the cooling towers and fly ash and bottom ash sluicing operations.

Three major task areas performed in this study include:

1) Existing Operations Modeling,

2) Alternatives Modeling, and

3) Economics.

The results of the existing operations simulations of the cooling towers compare well to the sample data obtained at the plant. The calculated $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ relative saturations in the cooling tower water (0.1-0.3 and 2.5×10^{-4}, respectively) indicate that the cycles of concentration may be significantly increased without calcium sulfate (gypsum) scale. However, an increase in cycles of concentration will probably require treatment such as acid addition to control calcium carbonate scale.

Nine cooling tower simulations were performed to determine the degree of acid treatment necessary for increased cycles of concentration in the towers (to reduce tower blowdown quantity) and the effects of increased calcium levels in the cooling tower makeup water (operational effects of poorer quality makeup water). No scale potential for $CaSO_4 \cdot 2H_2O$ was identified in any of the cases. Sulfuric acid treatment was required for $CaCO_3$ scale control of all cases.

Table 1-1 presents a summary of the technically feasible options for the Bowen water system as compared to existing operations and the relative costs of each of these alternatives. Two process alternatives were studied for the

TABLE 1-1. SUMMARY OF TECHNICALLY FEASIBLE OPTIONS AT BOWEN

	Existing Condition	Alternative One	Alternative Two	Alternative Three
Cooling Tower Makeup Source	Makeup Pond, Service Water	Makeup Pond, Service Water	Makeup Pond, Service Water	Makeup Pond, Service Water, Brine Concentrator Distillate
Cycles of Concentration in Towers	1.7	5.7	15.	15.
Cooling System Treatment	None	H_2SO_4	H_2SO_4	H_2SO_4
Acid Addition Rate, kg/day[1] (lb/day)	0 (0)	481 (1060)	608 (1340)	608 (1340)
Ash Sluice Makeup Source	Cooling Tower Blowdown	Cooling Tower Blowdown	Cooling Tower Blowdown	Cooling Tower Blowdown
% Recycle in Fly Ash System	0	0	60	60
% Recycle in Bottom Ash System	0	0	100	100
Ash System Treatment	None	None	Recycle Softening	Recycle Softening, Brine Concentration of Pond Overflow
Plant Makeup Requirements, ℓ/sec (GPM)	3250 (51,500)	1880 (29,800)	1670 (26,400)	1630 (25,800)
Plant Discharge Rate, ℓ/sec (GPM)	1600 (25,000)	255 (4050)	41 (650)	0 (0)
Costs [2]				
Capital, 1976 $	--	100,000	1,223,000	6,380,000
Operating, 1976 $/yr [3] (mils/kw-hr)	--	52,900 (.002)	402,000 (.018)	1,735,000 (.078)

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[1] As 100% H_2SO_4.

[2] These rough cost estimates were made to compare technically feasible options and do not include a "difficulty to retrofit" factor.

[3] Includes capital cost amortization at 15% per year.

ash sluicing system at Bowen. The first case involved using cooling tower blowdown from the towers operating at 5.7 cycles of concentration to sluice both bottom and fly ash on a once-through basis at about 10 wt. % solids (Alternative 1 in Table 1-1). The effects of CO_2 mass transfer in the ash pond and sluice tank on the system operation were investigated. No gypsum scale potential was identified in any of the cases with once-through ash sluicing. It should be noted here that this analysis was performed to study general water recycle/reuse alternatives. Actual implementation of any of these alternatives would require a more extensive investigation of process parameter variability. More water quality data would be required along with additional studies to fully characterize the ash reactivity variations as a function of time.

Potential scaling of $CaCO_3$ is present in all cases studied. However, the fly ash slurry line possibly can be kept free of plugging by the addition of a fly ash slurry reaction tank and by frequent flushing with a water stream of pH 6-7. Pilot or bench scale testing is recommended to determine accurately the size of reaction tank and frequency and quantity of acid washing required or if other measures are necessary.

The second alternative for the ash sluicing system involved using cooling tower blowdown from the towers operating at 15.0 cycles of concentration as makeup water to a recirculating ash sluice system (Alternative 2 in Table 1-1). If the pond recycle water remains supersaturated with respect to gypsum, scaling will occur in this system. However, this situation may be remedied by chemical treatment. Sodium carbonate softening of approximately 80% of the pond recycle water will maintain a gypsum relative saturation of about 1.0 in the slurry line and prevent calcium sulfate scaling. The calcium carbonate sludge produced in the softening step may be disposed of in the ash pond. Problems may also be encountered in the cooling towers at 15 cycles with silica scale potential. Additional studies to determine control limits should be conducted before implementing this alternative.

Zero discharge from the cooling and ash sluicing systems (Alternative 3 in Table 1-1) may be achieved by installing a softening/reverse osmosis/brine concentration unit to treat the ash pond overflow (41 ℓ/sec or 650 GPM) and recycling approximately 50% of the clean water as boiler makeup and the remainder as cooling tower makeup.

As with the once-through operations, $CaCO_3$ and $Mg(OH)_2$ scale potential was noted but can probably be minimized by installing a reaction tank prior to the sluice line and frequent flushing of the line with a pH 6-7 water stream.

The rough cost estimates presented for the alternatives in Table 1-1 indicate that reducing the ash pond overflow to 225 ℓ/sec(4050 GPM) by running the cooling towers at 5.7 cycles of concentration and sluicing the ash on a once-through basis using cooling tower blowdown is the less expensive option (about $100,000 capital cost with about $53,000/yr operating costs). This option necessitates acid treatment in the towers.

Reducing the ash pond overflow to about 41 ℓ/sec (650 GPM) by operating the cooling towers at 15.0 cycles of concentration (with acid treatment) and using the tower blowdown as makeup to a recirculating ash sluice system (with Na_2CO_3 softening of 80% of the pond recycle) has an initial capital cost of about $1,223,000 and operating costs including capital cost amortization of about $402,000/yr. The inclusion of a softening/reverse osmosis/brine concentrator unit to eliminate the ash pond overflow discharge (recycle to boiler and cooling tower makeup) for this alternative would require a capital investment of about $6.38 million total. The additional operating costs would be about $1,333,000/yr, giving a total of approximately $1,735,000/yr.

Detailed discussions of the existing operations simulations, the alternative simulations, and the rough cost estimates constitute the main body of this appendix.

2.0 PLANT CHARACTERISTICS

Plant Bowen is a four-unit 3,180 Mw coal-fired electric generating station located near Taylorsville, Georgia. The coal utilized at Bowen is approximately 11% ash and 2.8% sulfur with a heating value of about 11,500 Btu/lb. The plant employs cooling towers and once-through bottom and fly ash wet sluicing for all of the units.

This section of the appendix describes the analysis of Plant Bowen's water system. First, an overall plant water balance is presented which shows the major in-plant flows and chemical analyses for the streams which were sampled. Then a detailed description of each of the major water consumers in the plant is given. This is followed by a brief discussion of the process model and the input data used to simulate existing operations at Plant Bowen. The computer simulation results are finally presented and discussed. This discussion will include a comparison of the simulation results and the chemical analyses of the samples taken. Areas which show a potential for water recycle/reuse will be identified and discussed.

2.1 Water Balance

A flow schematic for the Bowen water system is shown in Figure 2-1. The major streams in the plant, including the cooling tower and ash handling systems, are shown in this diagram. The numbers in the diamonds refer to the stream numbers shown below the schematic where the design flows and results of the chemical analyses of the spot samples taken at Bowen are presented. A more detailed description of the samples taken and analytical procedures used is presented in Appendix B.

Makeup water for the plant is taken from the Etowah River and stored in a makeup pond. Water is removed from the makeup pond at a design rate of 3,280 ℓ/sec (52,000 GPM) and used as general service water, boiler makeup, and cooling tower makeup.

The general service water effluent is split so that 5% of the flow returns to the makeup pond and 95% is used as cooling tower makeup. Water treatment wastes (not shown in Figure 2-1) total about 9.5 ℓ/sec (150 GPM) and are pumped to the ash pond. The major water consumers at the Bowen plant are the cooling tower system and the ash handling systems, which are discussed in the following sections.

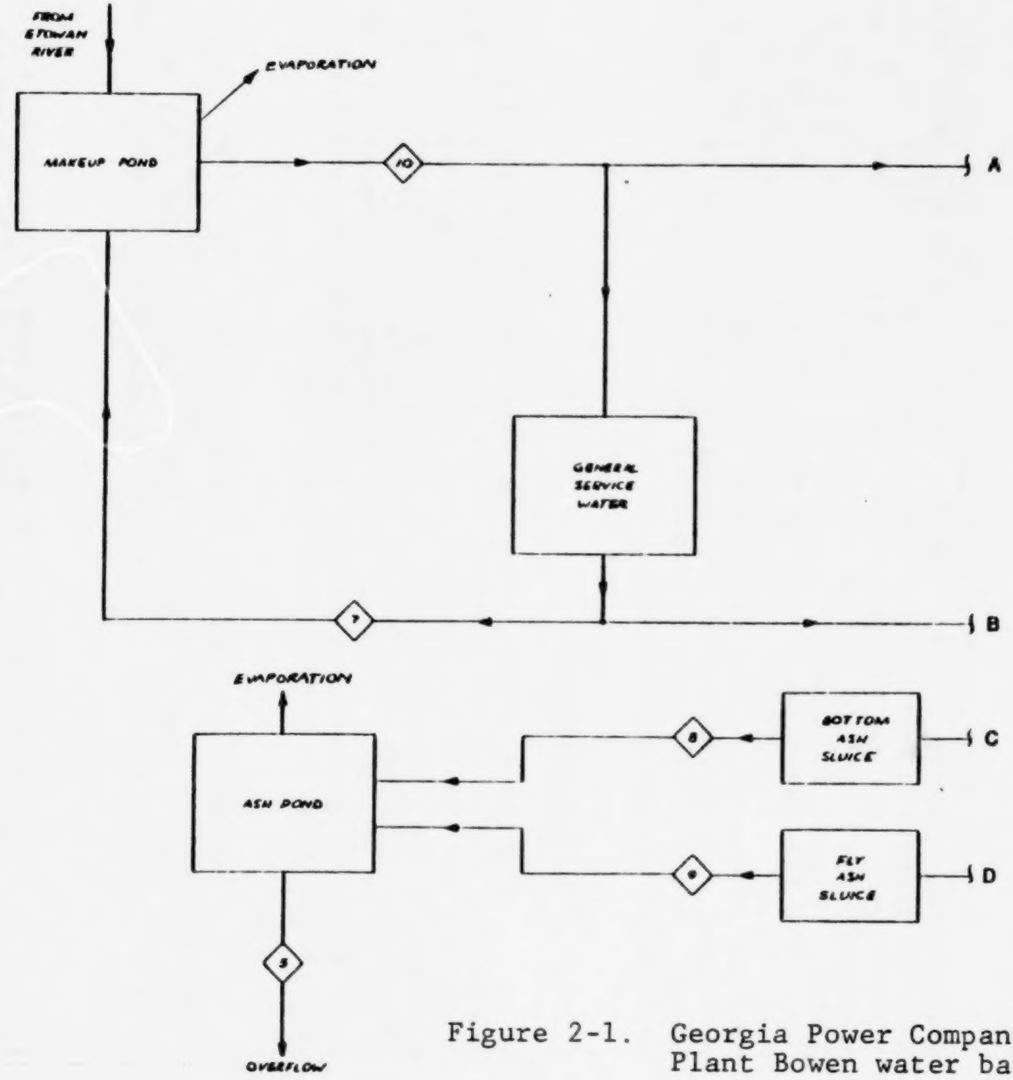


Figure 2-1. Georgia Power Company Plant Bowen water balance.

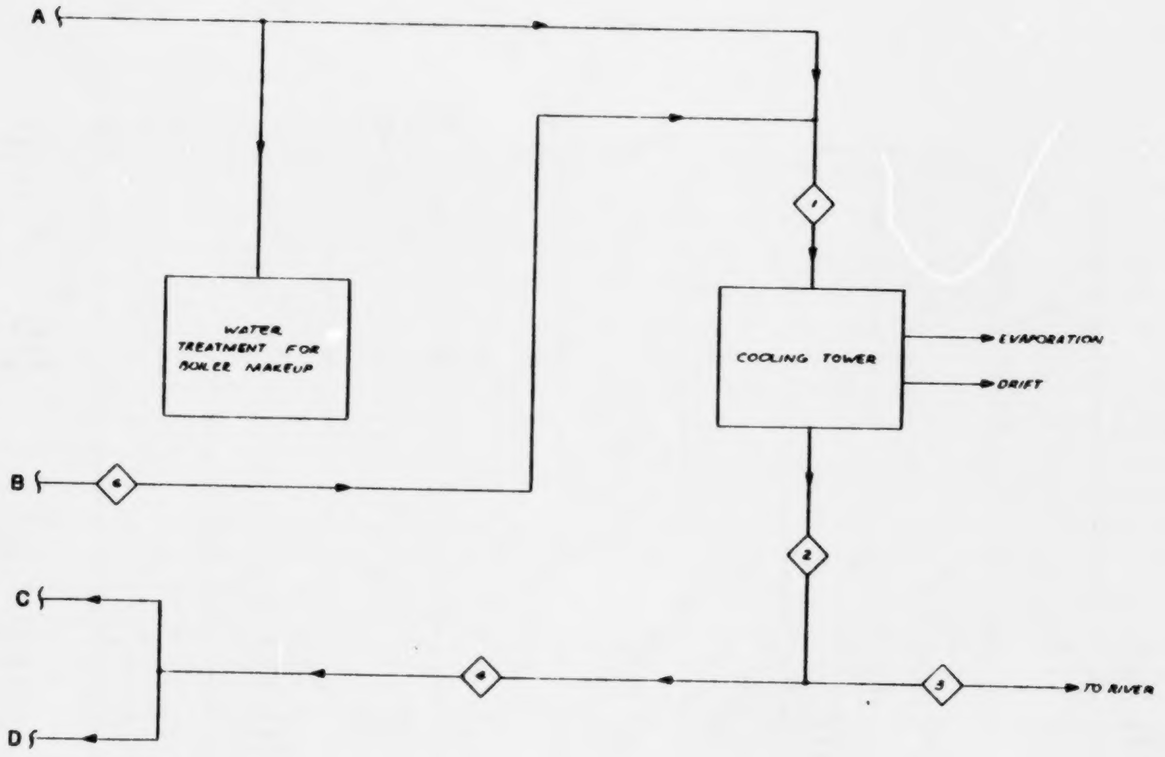


Figure 2-1. (Continued)

Stream Number	1	2	3	4	5	6	7	8	9	10
Stream Name	Cooling Tower Makeup	Cooling Tower Blowdown	Discharged Blowdown	Blowdown To Sluice Ash	Ash Pond Overflow	Service Water To Cooling Towers	Service Water Blowdown	Bottom Ash Sluice	Fly Ash Sluice	Plant Makeup Water
Flow: Metric English	3,230 ℓ/sec. 51,000 gpm	1,900 ℓ/sec. 30,000 gpm	320 ℓ/sec.* 5,000 gpm*	1,580 ℓ/sec.* 25,000 gpm	1,580 ℓ/sec. 25,000 gpm	670 ℓ/sec. 10,500 gpm	35 ℓ/sec. 550 gpm	1,230 ℓ/sec.* 19,500 gpm	350 ℓ/sec. 5,500 gpm	3,280 ℓ/sec. 52,000 gpm
pH	7.7	7.9	7.9	7.9	10.4			6.5	11.5	
Calcium	6.1	16.1	16.1	16.1	89			21.6	311	
Magnesium	1.7	2.1	2.1	2.1	1.7			2.3	<0.1	
Sodium	1.4	0.2	0.2	0.2	19.6			1.5	9.4	
Potassium	<0.4	<0.4	<0.4	<0.4	5.4			1.5	19.8	
Chloride	2.1	6.4	6.4	6.4	8.2			3.5	3.9	
Carbonate (as CO_3)	20.4	43.0	43.0	43.0	24			39	22	
Sulfate (as SO_4)	1.9	3.0	3.0	3.0	182			38.4	514	
Nitrate (as NO_3)	4.0	8.4	8.4	8.4	11.2			5.2	9.5	
Phosphate (as PO_4)	<0.1	<0.1	<0.1	<0.1	<0.1			<0.1	<0.1	
Silicates (as SiO_3)	25	28	28	28	55			30		
Suspended Solids	<0.01	<0.01	<0.01	<0.01	<0.01			1.11	7.0	
Dissolved Solids	57	93	93	93	374			139	1,370	

*These stream flows vary due to the periodic sluicing of bottom ash. The value shown for Stream 8 assumes full load operation and was obtained as the difference between the cooling tower blowdown and the fly ash sluice water. Excess cooling tower blowdown, when not used for ash sluicing, is discharged (Stream 3).

Figure 2-1. (Continued)

The first step in characterizing the chemistry of the Bowen water system is to examine the results of the spot samples taken. The measured species concentrations were input to the equilibrium program and several parameters were calculated which determine the tendency of the liquor sampled to form chemical scale and to absorb or desorb CO_2 from the atmosphere. Another parameter calculated checks the internal consistency of the sample and is a measure of the analytical accuracy.

Table 2-1 presents a summary of the parameters calculated for each of the samples taken at Bowen. Relative saturations for $CaCO_3$, $Mg(OH)_2$, and $CaSO_4 \cdot 2H_2O$ are given in the first three columns. These parameters indicate the tendency of the stream to form scale. Critical values for relative saturation of each species, above which scale formation is likely, are 2.5 for $CaCO_3$, 3.4 for $Mg(OH)_2$, and 1.3-1.4 for $CaSO_4 \cdot 2H_2O$ (see Appendix C).

None of the streams sampled showed a tendency to form $Mg(OH)_2$ or $CaSO_4 \cdot 2H_2O$ scale. The highest gypsum relative saturation was 0.28 in the fly ash slurry water, well below the critical range of 1.3-1.4. Three of the seven streams sampled showed $CaCO_3$ relative saturations greater than the critical value of 2.5. The fly ash sluice and pond samples showed $CaCO_3$ relative saturations of 17.1-38.8. The decrease in relative saturation from the fly ash sluice to the pond is most probably a result of $CaCO_3$ precipitation and/or CO_2 absorption from the atmosphere.

The equilibrium partial pressures shown in Table 2-1 are an indication of the tendency of a liquor to absorb or desorb CO_2 when in contact with the atmosphere. A value less than 3×10^{-4}, the equilibrium partial pressure of CO_2 in air, indicates a tendency to absorb CO_2 and a value greater indicates a tendency to desorb CO_2. The value for the fly ash sluice water is 7×10^{-10} atm indicating a strong tendency to absorb CO_2. The value for CO_2 partial pressure of the pond water, 2×10^{-7}, is larger than the fly ash sluice but still less than atmospheric which indicates that some CO_2 transfer is occurring in the pond but that complete equilibrium is not achieved. The value for the cooling tower blowdown sample is about 5×10^{-4} indicating that the cooling tower blowdown CO_2 concentration is very near the equilibrium value.

TABLE 2-1. PARAMETERS CALCULATED BY EQUILIBRIUM PROGRAM FOR BOWEN SAMPLES

Stream Name	Stream Number	Relative Saturations*			Equilibrium partial pressure of CO_2, atm	% Residual Electroneutrality
		$CaCO_3$	$Mg(OH)_2$	$CaSO_4 \cdot 2H_2O$		
Cooling Tower Makeup	1	0.016	6.3×10^{-7}	1.0×10^{-4}	3.95×10^{-4}	-4.0
Cooling Tower Blowdown	2	0.15	2.8×10^{-6}	3.0×10^{-4}	5.33×10^{-4}	-12.8
Bottom Ash Sluice	8	0.01	3.2×10^{-8}	5.0×10^{-4}	9.5×10^{-3}	-5.0
Fly Ash Sluice	9	38.8	---	0.28	7.0×10^{-10}	-3.9
Ash Pond Subsurface	-	17.4	0.065	0.056	2.0×10^{-7}	+10.0
Ash Pond Effluent	5	17.1	0.065	0.058	2.0×10^{-7}	+4.0
Plant Drainoff Water	-	0.31	1.7×10^{-5}	0.003	1.15×10^{-4}	+6.0

* Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$, about 2.5 for $CaCO_3$, and about 3.4 for $Mg(OH)_2$ (see Appendix C).

The last parameter shown in Table 2-1, % residual electroneutrality, is calculated to determine the internal consistency of each sample with pH specified. A value of ±15% is considered acceptable. All of the Bowen samples were within this range. A more detailed description of how this parameter is calculated is presented in Appendix E.

2.2 Cooling Tower System

Each of the four units at Plant Bowen have independent cooling systems with one cooling tower for each unit. Units 1 and 2 are identical (700 Mw) and have identical cooling towers. Units 3 and 4 are each rated at 880 Mw and also have identical cooling towers. Water circulates between the condenser and the cooling tower of each unit at a rate of 16,280 ℓ/sec (258,000 GPM) for Units 1 and 2 and 19,530 ℓ/sec (310,000 GPM) for Units 3 and 4. A blowdown stream is removed from the circulating water after the condenser. The water removed as blowdown is replenished with fresh makeup water.

The blowdown rate is maintained so that the dissolved species concentrations remain low enough to prevent scaling in the condenser. The relationship between the blowdown rate, the cooling tower evaporation rate, the drift rate, and the amount of concentration that dissolved species undergo is expressed below:

$$C = \frac{E + B + D}{B + D} \qquad (2\text{-}1)$$

where

C = cycles of concentration

E = evaporation rate

B = blowdown rate

D = drift rate

Present operation of the Bowen cooling system maintains the blowdown rate so that the makeup water is concentrated about 1.7 times (i.e., $C \cong 1.7$). This allows the towers to operate scale-free without acid addition to control pH. Excess blowdown is discharged.

2.2.1 Simulation Basis

Existing cooling tower operations at Plant Bowen were simulated to verify the model validity so that water recycle/reuse alternatives can be evaluated. These simulations will also help identify potential areas for recycle/reuse of water at Plant Bowen. This section presents the basis for simulating existing operations for the cooling towers at Bowen. First, the process model used is briefly described followed by a presentation of the input data. A detailed description of the process model is included in Appendix E.

The existing operations of the Bowen water system were simulated by means of the computer model shown in Figure 2-2. This is a generalized cooling tower model with capabilities of simulating sulfuric acid addition and slipstream softening for calcium removal. Neither option was used for existing operations.

Given the inputs of air flow, temperature and composition, makeup water composition, flow and temperatures of the circulating water, drift rate, and cycles of concentration, the model performs iterative calculations around the cooling loop to determine the blowdown, evaporation and makeup rates, and compositions for all water streams. An acid addition rate (if required) is determined to keep the $CaCO_3$ relative saturation within a specified range. If slipstream softening is required (determined by model) the slipstream and chemical addition rates are calculated.

Several assumptions are inherent in performing this simulation with the subroutines outlined above. These assumptions are enumerated below:

1) Equilibrium exists between CO_2 and H_2O in the atmosphere and cooling tower exit water.

2) The temperature of the cooled water stream approaches the wet bulb temperature of ambient air within a predictable range.

3) The compositions and temperatures of the cooled water and drift streams are equal.

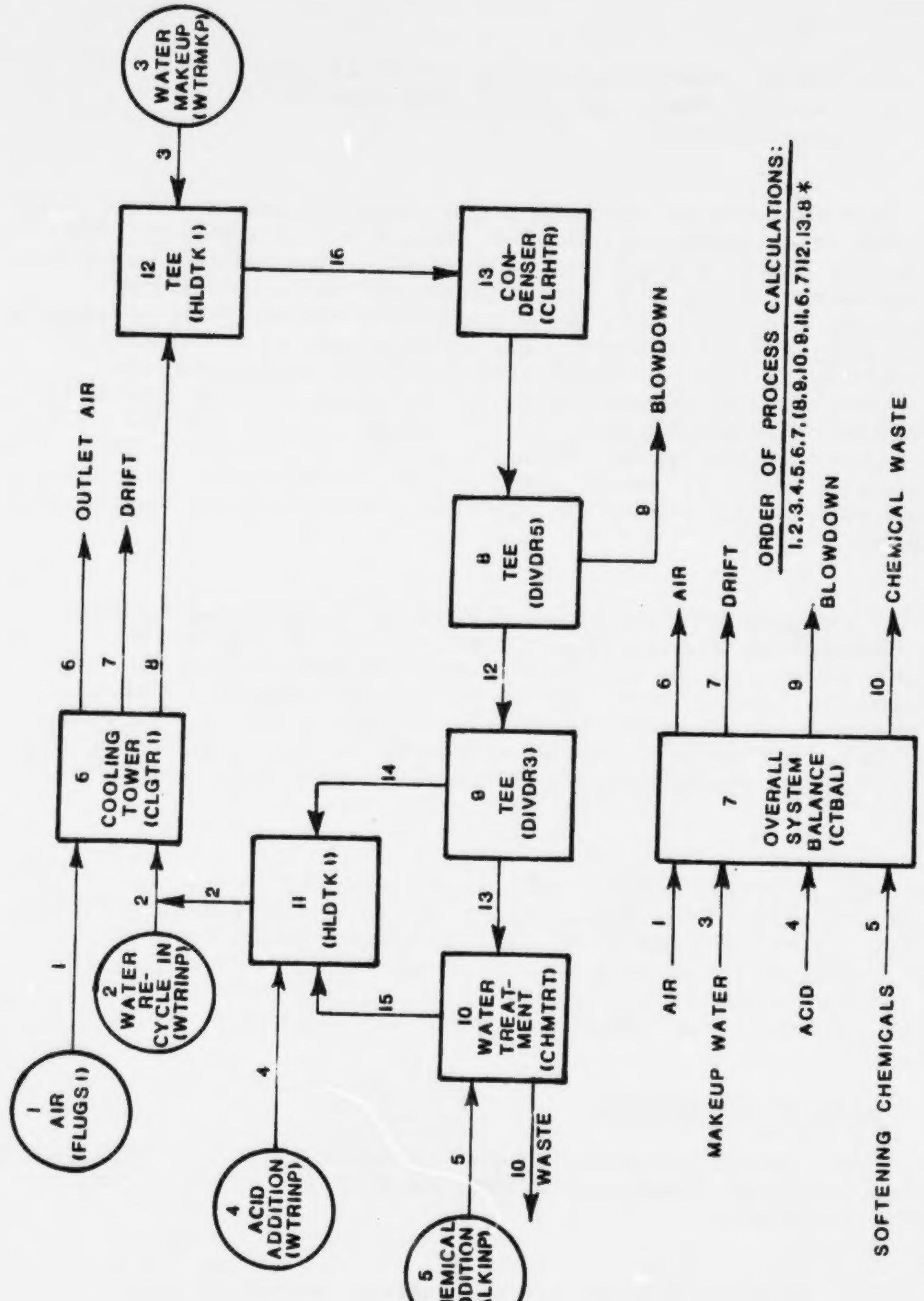


Figure 2-2. Process simulation scheme for Bowen cooling tower system.

4) Ionic reactions taking place in the liquid phase are rapid and thus at equilibrium.

The assumption involving the temperature of the cooled water stream is a recognized design parameter in cooling tower evaluation and gives a good approximation. The assumption concerning the temperature and composition of the drift stream should be very close to actuality as is the assumption in regard to H_2O gas-liquid equilibrium. The assumption with regard to CO_2 equilibrium is conservative since the partial pressure of CO_2 in actual cooling towers tends to be greater than the equilibrium value. The assumption in the model causes the pH to be slightly higher in the model than in actual operation. The higher pH causes the relative saturation of $CaCO_3$ to increase more than the lowered carbonate species concentration causes it to decrease.

A summary of the input stream data employed in the existing operations simulations is presented in Table 2-2. The cooling tower design air flows were obtained from GPC and adjusted to the temperature and water content shown. The air temperature and composition were calculated using local climatological data for Atlanta between December, 1974, and November, 1975. The makeup water composition was obtained from chemical analyses.

The cooling tower drift rate, approach, cycles of concentration, and circulating water flow were obtained directly from GPC or calculated from data obtained from GPC. The condenser temperature change was also obtained from GPC. The ambient air wet bulb temperatures were derived from Atlanta climatological data for December, 1974, to November, 1975.

2.2.2 Simulation Results

This section describes the results from the simulation of existing cooling tower operations at Bowen. Three simulations were performed:

1) Cooling Towers 1 & 2, Summer Operation

2) Cooling Towers 1 & 2, Winter Operation

3) Cooling Towers 3 & 4, Summer Operation

TABLE 2-2. INPUT DATA FOR BOWEN COOLING TOWER SIMULATIONS

	Units 1 & 2		Units 3 & 4
	Summer	Winter	Summer
FLOWS			
Air, m^3/hr	2.46×10^7	3.6×10^7	3.52×10^7
(ACFM)	(1.45×10^7)	(2.12×10^7)	(2.07×10^7)
Drift, ℓ/sec	3.3	3.3	3.9
(GPM)	(52)	(52)	(62)
Circulating Water, ℓ/sec	16,300	16,300	19,500
(GPM)	(258,400)	(258,400)	(310,000)
TEMPERATURES			
Ambient Air, °C	23.9	7.8	23.9
(°F)	(75)	(46)	(75)
Approach, °C	10.6	10.6	10.0
(°F)	(19)	(19)	(18)
Condenser ΔT, °C	14.2	14.2	15.6
(°F)	(25.6)	(25.6)	(28)
Wet Bulb, °C	21.1	5.6	21.1
(°F)	(70)	(42)	(70)
Condenser Outlet, °C	46.1	30.6	46.7
(°F)	(115)	(87)	(116)
ADDITIONAL DATA			
Relative Humidity, %	78.0	73.0	78.0
Cycles of Concentration	1.7	1.7	1.7
Makeup Water Composition, mg/ℓ			
Calcium	6.0	6.0	6.0
Magnesium	1.7	1.7	1.7
Sodium	1.4	1.4	1.4
Chloride	2.1	2.1	2.1
Carbonate, as $CO_3^{=}$	20.4	20.4	20.4
Sulfate, as $SO_4^{=}$	1.9	1.9	1.9
Nitrate, as NO_3^{-}	4.3	4.3	4.3

The simulation results will be compared to the chemical analyses results from the samples gathered at Bowen in order to evaluate the validity of the process model. These simulations will be used to discuss possible water recycle/reuse alternatives at Bowen, and potential problems which could be caused by implementing alternatives will be discussed.

A summary of the simulation results for existing cooling tower operations at Bowen is presented in Table 2-3. The first column in Table 2-3 shows a summary of actual plant data concerning the cooling tower blowdown characteristics for cooling tower number 3. Process simulations were performed for the summer and winter operation of towers 1 and 2 and the summer operation of towers 3 and 4.

The cooling tower blowdown pH value of 7.93 for the simulated operation (Case 3) compares very well to the measured value of 7.9.

Comparison of some of the sample data with simulation results indicates that the system may not have been at steady state during sampling. For example, measured calcium and chloride concentrations are higher than the computed values whereas magnesium and sodium measured concentrations are lower than the simulation results. These discrepancies may also be due to nonhomogeneous sampling and/or analytical errors as well as unsteady-state operation.

The sulfate and nitrate concentrations measured compare favorably with the simulated values. The calcium carbonate relative saturations are consistent in that the system is operating well below the critical level for scaling of 2.5 (see Appendix C).

Calcium carbonate relative saturation is very dependent on pH due to the carbonate-bicarbonate-carbonic acid equilibrium in solution and accounts for the differences shown. This dependence on pH is illustrated by comparing the values for Case 2 to the values for Case 3. The blowdown concentrations are approximately the same, yet the respective relative saturations are 0.11 and 0.30. The lower pH of 7.87 as opposed to 7.93 is enough of a difference to lower the relative saturation from 0.30 to 0.11, even with a slightly higher carbonate concentration in Case 2.

TABLE 2-3. BOWEN EXISTING COOLING TOWER OPERATIONS

Cooling Tower Blowdown	Plant Data (Tower No. 3)	Simulations Case 1 Towers 1&2 Summer	Simulations Case 2 Towers 1&2 Winter	Simulations Case 3 Towers 3&4 Summer
Flow, ℓ/sec per tower (GPM)	442 (7,000)	467 (7,400)	391 (6,200)	625 (9,900)
pH	7.9	7.94	7.87	7.93
Composition, mg/ℓ				
Calcium	16.1	10.3	10.2	10.3
Magnesium	2.1	2.9	2.9	2.9
Sodium	0.2	2.3	2.3	2.3
Chloride	6.4	3.6	3.6	3.6
Carbonate, as $CO_3^{=}$	43.0	33.8	34.3	33.8
Sulfate, as $SO_4^{=}$	3.0	3.3	3.3	3.3
Nitrate, as NO_3^{-}	8.4	7.4	7.4	7.4
Relative Saturations *				
$CaCO_3$	0.15	.30	.11	.30
$CaSO_4 \cdot 2H_2O$	3.0×10^{-4}	2.5×10^{-4}	2.4×10^{-4}	2.5×10^{-4}
Partial Pressure CO_2, atm	5.33×10^{-4}	5.63×10^{-4}	5.11×10^{-4}	5.89×10^{-4}

* Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C).

The low measured calcium sulfate relative saturations are confirmed by the simulation results. The critical value of relative saturation for scaling of calcium sulfate to occur is 1.3-1.4.

These simulations indicate a potential for reducing water requirements and discharges for the cooling towers by increasing the cycles of concentration but not so much as to reach the critical scaling level for calcium carbonate. If acid treatment for calcium carbonate scale control is instituted in the Bowen cooling tower system, the cycles of concentration may be increased until calcium sulfate or some other species such as $CaHPO_4(s)$ reaches the respective critical value for scaling. The decreased cooling tower blowdown resulting from operation at higher cycles of concentration might then be used for ash sluicing on a once-through basis or in a recirculating system.

The effects of increased cycles of concentration on cooling tower blowdown and the subsequent use of the cooling tower blowdown in an ash sluicing system are discussed in Section 3.0. The effects of increased calcium in the makeup water are also investigated to determine the operational effects of poorer quality makeup water.

2.3 Ash Handling Systems

Fly ash is collected by electrostatic precipitators at a rate of about 24,200 kg/hr (53,300 lb/hr) from Units 1 and 2 and about 22,500 kg/hr (49,500 lb/hr) from Units 3 and 4. The total rate of collection is therefore about 93,400 kg/hr (205,600 lb/hr). The collected fly ash is sluiced on a once-through basis to the ash pond using cooling tower blowdown as sluice water. Sluicing this amount of fly ash at about 7% solids (see sample analyses in Figure 2-1) requires 350 ℓ/sec (5,500 GPM) of water. Detailed calculations showing how the fly ash rates and water rates were obtained are presented in Appendix K.

Bottom ash is periodically sluiced with cooling tower blowdown to the ash pond also on a once-through basis. The remainder of the cooling tower blowdown that is not used for sluicing fly ash is used to sluice the bottom ash at about 1% solids (see sample analyses in Figure 2-1). This water is discharged when it is not used to sluice the bottom ash.

2.3.1 Simulation Basis

Existing operations of the Bowen fly ash sluicing system were simulated by means of the computer model shown in Figure 2-3. This was done to verify the model and establish a basis for comparison. The model uses information about the composition and flows of the makeup water and the fly ash as well as the percent solids in the sludge and pond evaporation as inputs. From this information the flows and compositions of all the streams are calculated. A detailed description of the ash sluicing model is given in Appendix E.

Several assumptions were made in modeling the ash sluicing system with this simulation. These include:

1) Solid-liquid equilibrium is achieved in the ash pond, with the exception of $CaSO_4$ which is allowed to remain supersaturated.

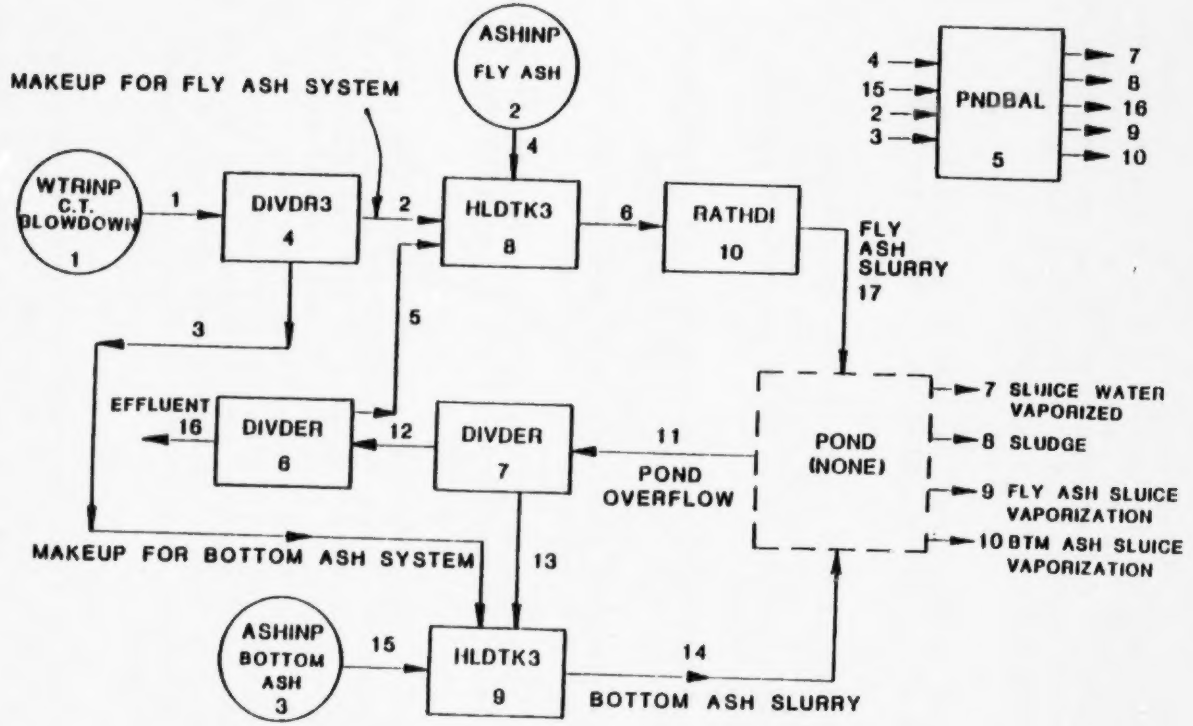
2) Ash dissolution is essentially complete before the slurry reaches the pond.

3) All solids precipitation occurs in reaction vessels or the pond.

4) Ionic reactions taking place in the liquid phase are rapid and thus at equilibrium.

The input data required to simulate the once-through ash sluicing system at Bowen are presented in Table 2-4. Sluice water rates were calculated based on a fly ash slurry solids content of about 7 wt. % and a bottom ash slurry solids content of about 1 wt. %. The pond evaporation rate was calculated based on average wind speed, ambient air composition, pond surface area, and pond surface temperature. The sluice water composition (cooling tower blowdown) was obtained from the results of the existing operations cooling tower simulation previously discussed.

The fly ash flow rate was obtained from precipitator inlet and outlet grain loadings obtained from GPC. The bottom ash flow was calculated as the difference between the total ash from the coal and the fly ash. The soluble species data for the fly ash were obtained from ash characterization studies performed in support of this program (see Appendix L). Calculations performed in obtaining this input data are explained in Appendix K.



ORDER OF PROCESS CALCULATION: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 *

Figure 2-3. Process simulation scheme for Bowen ash sluicing system.

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TABLE 2-4. BOWEN EXISTING ASH SLUICING INPUT DATA

FLOWS (Unit 3)	
Fly Ash, kg/min (lb/min)	375.1 (825.3)
Bottom Ash, kg/min (lb/min)	205.3 (451.7)
Fly Ash Sluice Water, ℓ/sec (GPM)	83.3 (1320.0)
Bottom Ash Sluice Water, ℓ/sec (GPM)	340.0 (5387.0)
Pond Evaporation*, ℓ/sec (GPM)	1.1 (18)
SLUICE WATER COMPOSITION	
Cooling Tower Blowdown @ 1.7 cycles, mg/ℓ	
Calcium	10.2
Magnesium	2.9
Sodium	2.4
Chloride	3.6
Carbonates, as $CO_3^=$	33.8
Sulfates, as $SO_4^=$	3.3
Nitrates, as NO_3^-	7.4
POND DEPOSITS, wt. % solids	40.0
SOLUBLE FLY ASH SPECIES, wt. %	
CaO	0.21
MgO	0.0
Na_2O	0.15
$CaSO_4$	1.25

* for entire plant.

2.3.2 Simulation Results

Two simulations were performed for existing ash slurry operations at Bowen. The first did not allow CO_2 transfer in the ash pond and the second allowed the CO_2 in the pond to come to equilibrium with the atmosphere.

Table 2-5 presents the results of these simulations. The compositions of the pond liquor and the fly ash slurry sampled at the plant are compared to those predicted by the model.

The results for the fly ash slurry stream show that the model predicted higher calcium and sulfate values than the sample showed resulting in a slightly higher gypsum relative saturation (0.38 versus 0.28). A calcium carbonate relative saturation about three times that of the plant data was predicted by the model due to the higher calcium and carbonate values predicted. Since the sluice water carbonate concentration was 43 mg/ℓ (plant data for cooling tower blowdown) some calcium carbonate precipitation is indicated although no scale buildup has been reported for Bowen. The erosive character of the ash slurry may be preventing the buildup of scale by scrubbing the sluice pipe walls. Once the liquor reaches the pond, there is little solid-liquid mixing, which may account for the high $CaCO_3$ relative saturation calculated based on the pond sample.

The pond liquor results show that actual operation at Bowen is closer to no CO_2 transfer in the pond since the sample pH is 10.4 and the predicted values are 10.8 for no CO_2 transfer and 8.2 for CO_2 equilibrium. The differences in composition may be attributed to non-steady-state operation. Due to the long residence time in the pond, any process changes result in very slow system response. Thus, the pond liquor composition may vary in time with changes in the fly ash reactivity, slurry solids content and load, but the variations will be damped and will correspond more closely to a time averaged composition than a spot sample.

TABLE 2-5. BOWEN EXISTING ASH SLUICING OPERATIONS

	Fly Ash Slurry		Pond Liquor		
	Plant Data	Model	Plant Data	Model (No CO_2 Transfer)	Model (CO_2 Equilibrium)
Composition, mg/ℓ					
Calcium	311.0	405.0	89.0	65.6	72.2
Magnesium	<0.1	2.9	1.7	2.6	2.9
Sodium	21.2	2.4	22.8	2.4	2.4
Chloride	3.9	3.7	8.2	3.7	3.7
Carbonates, as $CO_3^{=}$	22.0	34.1	24.0	1.0	54.3
Sulfates, as $SO_4^{=}$	514.0	674.0	182.0	135.0	135.0
Nitrates, as NO_3^{-}	9.5	7.5	11.2	7.5	7.5
pH	11.5	11.0	10.4	10.8	8.2
Relative Saturations*					
$CaCO_3$	38.8	104.4	17.1	1.0	1.0
$Mg(OH)_2$	---	39.4	.065	1.0	7.3×10^{-6}
$CaSO_4 \cdot 2H_2O$	0.28	0.38	0.058	0.038	0.041
Equilibrium Partial Pressure of CO_2, atm	7×10^{-10}	1×10^{-8}	2×10^{-7}	2.1×10^{-9}	3×10^{-4}

* Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$, about 2.5 for $CaCO_3$, and about 3.4 for $Mg(OH)_2$ (see Appendix C).

3.0 TECHNICAL ALTERNATIVES

A modular approach to studying water recycle/reuse alternatives at Bowen was used in that the major plant water systems were divided into two subsystems to form separate process simulations. One subsystem consists of the cooling towers with associated treatment facilities (where necessary), hold tanks, and condensers. The other sybsystem consists of the ash handling systems. The studies for each subsystem will be discussed separately. The effects of increasing the cycles of concentration in the cooling towers and of poorer quality makeup water (increased calcium levels) are presented first. Then the use of cooling tower blowdown in a once-through and a recirculating ash sluice system is evaluated. The effects of carbon dioxide mass transfer between the atmosphere and the pond liquor are also investigated.

3.1 Cooling Tower System

The existing operations simulations indicated that the cycles of concentration may be greatly increased in the cooling towers without scaling with respect to calcium sulfate, but only limited increases in the cycles of concentration may be implemented before calcium carbonate reaches saturation. However, calcium carbonate scaling potential can be controlled with acid treatment of the circulating water. This section first presents a description of the simulation bases used, then a discussion of the results with respect to increased cycles of concentration and calcium in the makeup water.

3.1.1 Simulation Basis

The process model used to simulate alternatives for cooling tower operation is identical to that used for existing operations (see Appendix E). Acid treatment for calcium carbonate scale control was implemented to keep the $CaCO_3$ relative saturation between 0.5 and 1.0.

A total of nine simulations were performed for alternative cooling tower operations. Three simulations were performed with the existing makeup water quality and cycles of concentration of 5.7, 10.0, and 15.0. Three simulations were conducted with the calcium concentration in the makeup water doubled, and three additional cases were run with the calcium level tripled. Cycles of concentration values used in these simulations were also 5.7, 10.0, and 15.0 so that correlations could be made using all nine runs. Since calcium carbonate relative saturation is the limiting factor of cycles of concentration and the carbonates are essentially fixed by being in equilibrium with the atmosphere, the acid requirements will correlate to the calcium levels. Any changes in the calcium concentration of the makeup water will necessitate changes in the acid addition rate. The increased calcium runs were performed to determine the magnitude of those changes.

All of the alternative cooling tower simulations were performed for summer operation of towers three and four since these conditions represent the case of maximum blowdown rates. Increased evaporation rates realized during the summer months necessitates an increase in blowdown rate over that required during the winter months to maintain a constant value for cycles of concentration.

The only changes in the input data for the first three alternative simulations are the values for cycles of concentration. The makeup water compositions used in the last six cooling tower simulations were changed from existing data by increasing the calcium concentration. It should be noted that the chloride concentrations were adjusted in addition to the calcium levels. This was done to maintain a solution pH in the same range as the existing makeup water.

3.1.2 Effect of Increased Cycles of Concentration

The simulation results from the first three alternative cooling tower operation runs are presented in Table 3-1 along with the results for existing operations. These three alternate simulations represent tower operation at 5.7, 10.0, and 15.0 cycles of concentration. Sulfuric acid treatment was required to control calcium carbonate scale potential for all three cases, confirming the indications of the existing operations simulations that only limited increases in cycles of concentration could be achieved without treatment.

The first alternate operating run (Case 4) was made with 5.7 cycles of concentration. Increasing the cycles from 1.7 to 5.7 will require acid treatment as shown in Table 3-1. However, no calcium sulfate scale potential will be realized since the relative saturation is 0.012, well below the critical scaling value of 1.3 - 1.4. Although the critical scaling value for relative saturation of $CaCO_3$ is about 2.5 (Appendix C), acid addition requirements were calculated based on keeping $CaCO_3$ subsaturated. This will minimize the effects of upsets in

TABLE 3-1. EFFECT OF INCREASED CYCLES OF CONCENTRATION IN BOWEN COOLING TOWERS*

	Existing Operation	Increased Cycles of Concentration		
Case No.	3	4	6	5
Cycles of Cencentration	1.7	5.7	10	15
Makeup Water Rate, ℓ/sec	1060	530	485	468
(GPM)	(16800)	(8400)	(7690)	(7420)
Acid Addition Rate, kg/day**	0.	481	567	608
(lb/day)	(0.)	(1060)	(1250)	(1340)
Blowdown				
Flow, ℓ/sec	625	89.8	45.0	27.5
(GPM)	(9900)	(1420)	(714)	(436)
pH	7.9	8.0	7.9	7.7
Composition, mg/ℓ				
Calcium	10.3	34.3	60.2	90.2
Magnesium	2.9	9.7	17.0	25.5
Sodium	2.3	7.9	13.8	20.7
Chloride	3.6	12.2	21.3	32.0
Carbonates (as $CO_3^=$)	33.8	39.2	32.1	20.9
Sulfates (as $SO_4^=$)	3.3	69.7	152	250
Nitrates (as NO_3^-)	7.4	24.8	43.4	65.0
Temperature, °C	46.7	46.7	46.7	46.7
(°F)	(116)	(116)	(116)	(116)
Relative Saturations***				
$CaCO_3$	0.30	0.97	0.94	0.51
$CaSO_4 \cdot 2H_2O$	2.5×10^{-4}	0.012	0.034	0.066

*All flows for Unit 3 or 4; the existing makeup water quality for summer months was used as a basis.

**As 100% H_2SO_4.

***Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C).

the system which might cause calcium and carbonate levels to reach the critical limit, such as increases in calcium content of the makeup water.

A cycles of concentration value of 5.7 for all towers will produce a blowdown rate for the plant of 312 ℓ/sec (4950 GPM) which will provide a once-through ash sluicing system at Bowen with enough water for a 10% solids ash slurry. The impact of using the blowdown water from the towers operating at 5.7 cycles of concentration will be discussed in Section 3.2.2.

Case 5 represents tower operation at 15.0 cycles of concentration. Even when the towers are operated at this high level of concentration, no scaling problems are noted as long as acid treatment is used for calcium carbonate scale control. The calcium sulfate relative saturation for Case 5 was only 0.066, still well below the critical level of 1.3 - 1.4. Acid requirements were increased by 127 kg/day (280 lb/day) from the calculated requirements of 481 kg/day (1060 lb/day) for operation at 5.7 cycles of concentration.

Case 6 was run to provide an additional data point for determining the effects of cycles of concentration on acid requirements for a given makeup water quality. The results from this run and Cases 4 and 5 are consolidated with the data obtained from the increased calcium cases in Section 3.1.3. Graphs depicting the effects of cycles of concentration and calcium in the makeup water on the acid requirements are presented.

Operating the cooling towers at higher cycles of concentration may cause species other than gypsum or calcium carbonate to become supersaturated and possibly form scale. Table 3-2 shows relative saturations for silica and phosphate solids in addition to the species already considered in the cooling tower blowdown at 15 cycles. None of the phosphate solids are above saturation but two silica solids are supersaturated. The SiO_2 relative saturation is 1.28 and the $Mg(SiO_2)_3(OH)_2$ (sepiolite) relative saturation is 14.0. These solids may cause problems at Bowen at 15 cycles of concentration but the respective critical values for these species are not known. The kinetics of the solid precipitation will determine if these solids will cause problems. Additional testing should be performed to determine the control limits for silica solids before implementing water recycle/reuse alternatives which require increased cycles of concentration in the

TABLE 3-2. RELATIVE SATURATIONS OF SCALE-FORMING SPECIES AT 15 CYCLES IN BOWEN COOLING TOWERS*

Species	Relative Saturation
$Ca(OH)_2$	1.5×10^{-9}
$CaCO_3$	0.52
$CaSO_4 \cdot 2H_2O$	0.066
$CaHPO_4$	0.031
$Ca_3(PO_4)_2$	2.2×10^{-3}
$Mg(OH)_2$	2.7×10^{-4}
$MgCO_3$	4.0×10^{-5}
SiO_2	1.28
$Mg(SiO_2)_3(OH)_2$	14.0
$Mg_3Si_2O_5(OH)_4$	0.36
CaH_2SiO_4	3.0×10^{-3}
$Ca(H_3SiO_4)_2$	0.075

*This simulation required an acid addition rate of 608 kg/day (1340 lb/day) towers. If necessary the silica concentration can be lowered by lime-soda ash or magnesium bicarbonate softening of either the makeup water or a slipstream from the circulating water (RO-266, TH-192).

3.1.3 Effect of Calcium Concentration in the Makeup Water

Six additional cooling tower simulations were performed. Three runs were made at cycles of concentration of 5.7, 10.0, and 15.0 with the calcium level in the makeup water tripled. Three runs with double calcium in the makeup water were also performed at cycles of 5.7, 10.0, and 15.0. The results from these six simulations are presented in Table 3-3. As in the cases presented in the previous section, acid addition rates were calculated to produce calcium carbonate relative saturations between 0.5 and 1.0, as shown in Table 3-3.

As can be seen from the relative saturations given in Table 3-3, even in the worst case (triple calcium, 15.0 cycles), scaling potential of calcium sulfate is nonexistent. The highest relative saturation was 0.13 (Case 9) which is significantly below the critical scaling level of 1.3 - 1.4.

Also shown in Table 3-3 is the acid addition rate expressed as a ratio of acid to calcium in the circulating water stream on a molar basis. This ratio is plotted versus cycles of concentration and calcium level in the makeup water in Figures 3-1 and 3-2. Data from Cases 4-12 were used to produce these graphs. As can be seen from these two graphs, the acid/calcium ratio decreases with increasing calcium in the makeup water and also with increasing cycles of concentration. This means that as the calcium level in the recirculating water increases, the acid/calcium ratio decreases, as shown in Figure 3-3. As calcium continues to increase, the slope of the curve in Figure 3-3 decreases sharply and the acid/calcium ratio approaches a constant value. This can be explained in the following way:

The relative saturation of calcium carbonate is defined by Equation 3-1:

$$R.S_{CaCO_3} = \frac{(a_{Ca^{++}})(a_{CO_3^{=}})}{Ksp_{CaCO_3}} \qquad (3\text{-}1)$$

TABLE 3-3. EFFECTS OF MAKEUP WATER CALCIUM CONCENTRATION ON BOWEN COOLING TOWER OPERATION

Case No.	7	8	9	10	11	12
Cycles of Concentration	5.7	10	15	5.7	10	15
Makeup Water Calcium, mg/ℓ	18	18	18	12	12	12
Blowdown						
Temperature, °C	46.7	46.7	46.7	46.7	46.7	46.7
(°F)	(116)	(116)	(116)	(116)	(116)	(116)
Composition, mg/ℓ						
Calcium	103	180	270	68.4	120	180
Magnesium	9.7	17.0	25.5	9.7	17.0	25.5
Sodium	7.9	13.8	20.7	7.9	13.8	20.7
Chloride	134	235	352	73.0	128	192
Carbonates (as $CO_3^{=}$)	17.9	15.5	18.9	22.6	24.1	21.2
Sulfates (as $SO_4^{=}$)	86.5	164	249	83.0	158	248
Nitrates (as NO_3^{-})	24.8	43.4	65.0	24.8	43.4	65.0
pH	7.6	7.5	7.6	7.7	7.7	7.7
Relative Saturations*						
$CaCO_3$	0.52	0.54	0.98	0.60	0.95	0.92
$CaSO_4 \cdot 2H_2O$	0.03	0.07	0.13	0.02	0.06	0.10
Acid Addition Rate, kg/day**	619	621	607	590	592	604
(lb/day)	(1365)	(1370)	(1340)	(1300)	(1305)	(1330)
Acid/Calcium Ratio x 10^3***	1.47	0.84	0.55	2.11	1.21	0.82

*Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C).

**100% H_2SO_4.

***Acid addition/calcium rate in circulating water (molar basis).

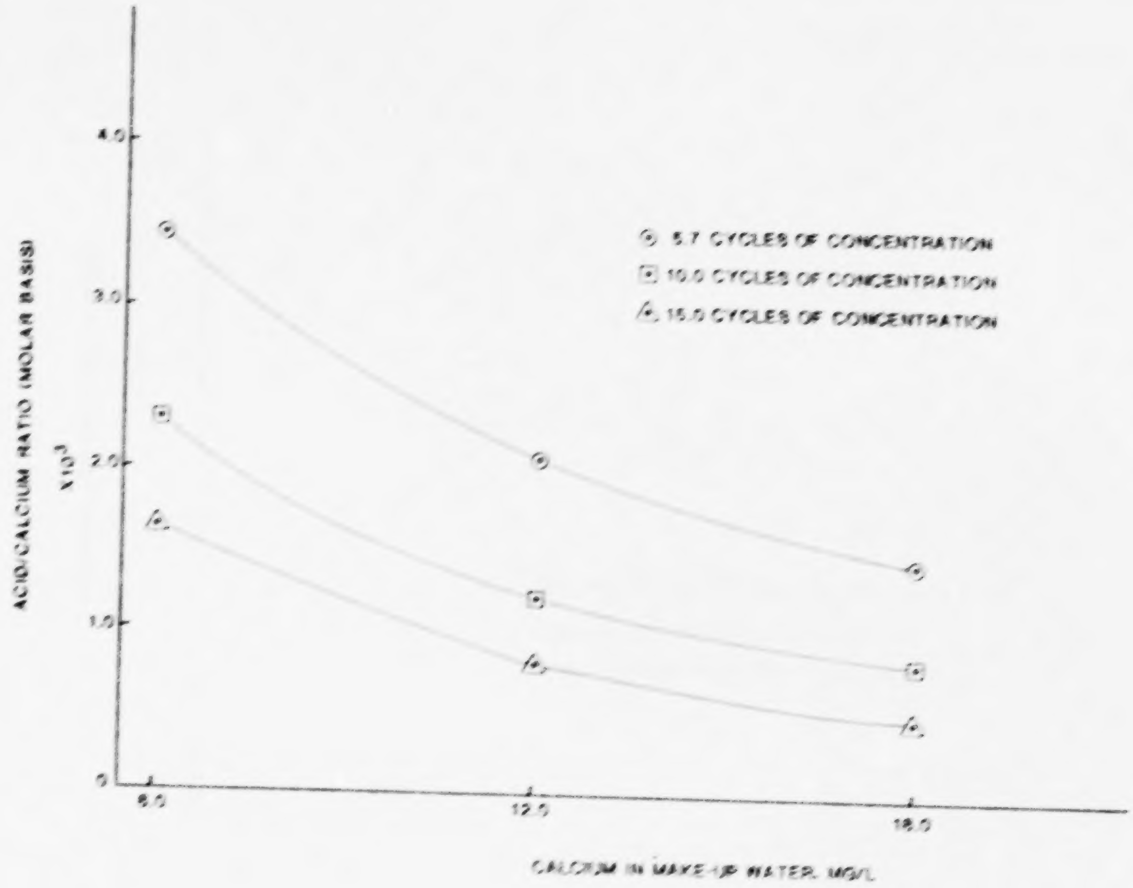


Figure 3-1. Acid requirements as a function of makeup water calcium.

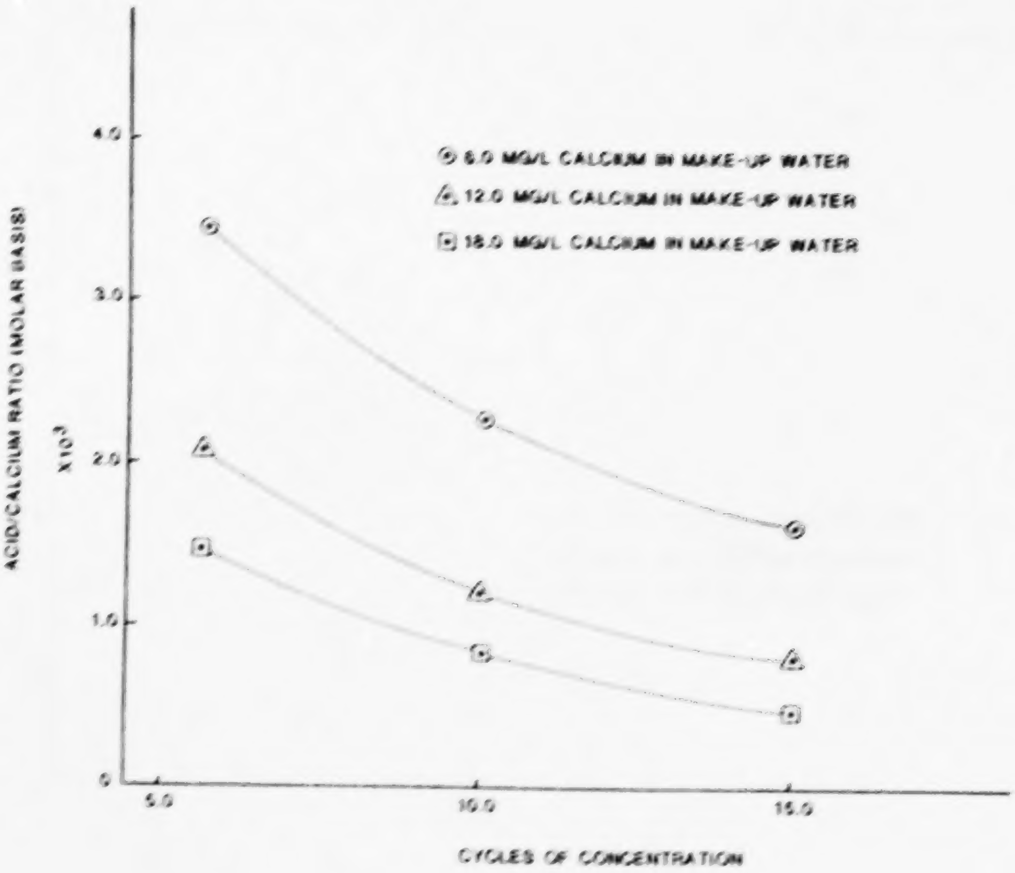


Figure 3-2. Acid requirements as a function of cycles of concentration.

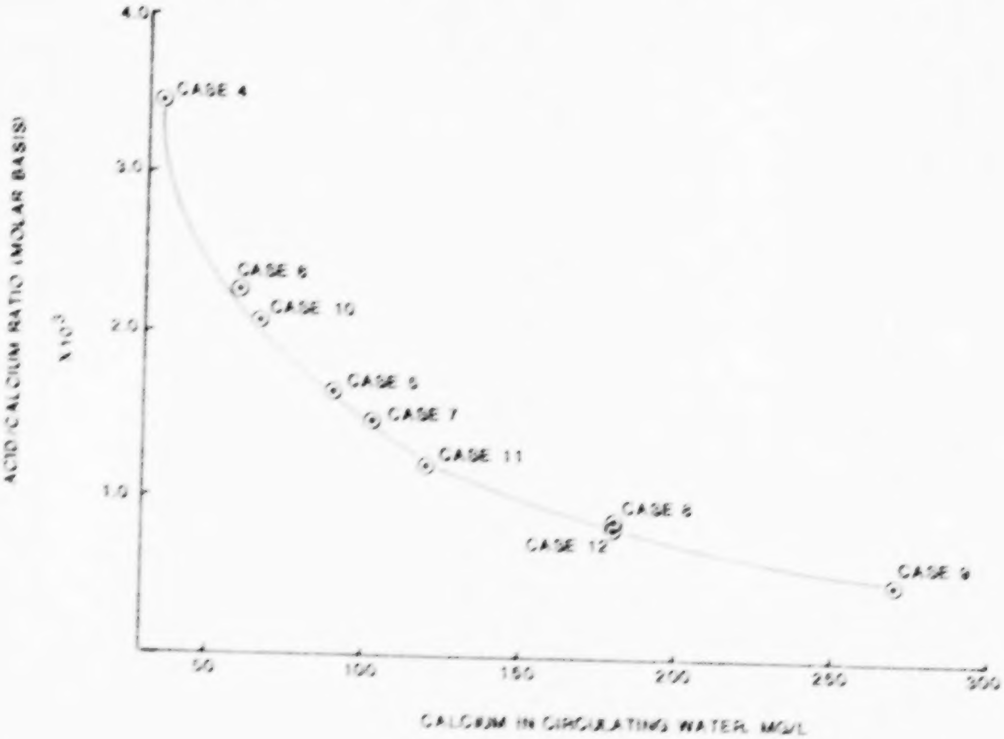


Figure 3-3. Acid requirements as a function of calcium in circulating water.

where $R.S_{CaCO_3}$ = relative saturation of calcium carbonate

$a_{Ca^{++}}$ = calcium ion activity

$a_{CO_3^=}$ = carbonate ion activity

$K_{sp_{CaCO_3}}$ = solubility product constant for calcium carbonate

As cycles of concentration increase, the ionic strength of the circulating liquor increases, resulting in increased ion pair formation which lowers the activity of the calcium ion. To keep a constant calcium carbonate relative saturation, the carbonate ion activity must be decreased at higher calcium levels but the lowering of the calcium ion activity at higher ionic strengths results in a decrease in acid addition per unit of total calcium.

For increased levels of calcium, the carbonate ion activity must decrease to keep the relative saturation constant and less than one. At these lower levels, the carbonate ion activity is roughly proportional to the solution pH and therefore roughly inversely proportional to the acid rate. If the calcium ion activities were directly proportional to the calcium concentrations, then the acid/calcium ratio would be a constant for high calcium levels. As calcium concentrations increase, however, the nonlinearities between the activity and the concentration become more substantial, resulting in the slight curvature observed in Figure 3-3. This slight curvature is also due to slight nonlinearities between the carbonate ion activity and the acid rate.

On the other hand, as calcium levels decrease, the carbonate ion activity must increase to keep the relative saturation constant. At higher carbonate activities, the acid rate is no longer linearly inversely proportional to the activity, resulting in the steep curvature observed at low calcium levels in Figure 3-3.

This curve may be used to determine theoretical acid addition rates for cooling tower operation at Bowen provided the circulating water rate and calcium concentration are known. For example, if the cooling tower is operating with 15,800 ℓ/sec (250,000 GPM) of circulating water with a calcium concentration of 150 mg/ℓ, the acid/calcium ratio determined from

Figure 3-3 is approximately 10^{-3}. The acid addition rate in gmoles/sec of 100% H_2SO_4 is then determined as follows:

$$\text{ACID} = 10^{-3}\ \frac{\text{gmole/sec } H_2SO_4}{\text{gmole/sec Calcium}} \times \frac{150 \text{ mg Ca}}{\ell} \times \frac{15{,}800\ell}{\text{sec}} \times \frac{\text{mmole Ca}}{40.1 \text{ mg Ca}} \times \frac{\text{gmole}}{1000 \text{ mmole}} = 0.059 \text{ gmoles/sec } H_2SO_4$$

It should be noted here that this curve applies only to the quality of makeup water sampled at Bowen with the calcium and chloride levels varied. Changes in magnesium, sulfate, or any other species that will have an effect on the level of chemical complexes formed in the system will affect the relative saturation of $CaCO_3$. The acid rate required may therefore depend on the concentrations of other species than calcium in the makeup water.

3.1.4 Summary of Cooling Tower Alternatives

The first set of simulations concerning increased cycles of concentration showed that with respect to $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ scale control the cycles may be increased to 15 easily which results in a 95.6% reduction in the cooling tower blowdown rate. However, at 15 cycles with the makeup water quality sampled, two silica solids are supersaturated, SiO_2 and $Mg(SiO_2)_3(OH)_2$ (sepiolite). The kinetics of these solids are not known so that additional testing should be performed to determine the control limits for these species.

The effects on cooling tower operation of the makeup water calcium concentration were determined and acid addition rates were correlated from the results of the remaining simulations performed. Even at 15 cycles with three times the calcium level of the makeup water sampled, no gypsum scale potential was identified.

3.2 Ash Handling Systems

For a system using cooling tower blowdown water exclusively as ash sluice water, the cycles of concentration in the tower system is determined by the water requirements of the ash sluice system. Two alternatives for ash handling at Bowen were studied:

1) once through sluice (10% solids)

2) recirculating sluice system

For each of these two alternatives, the effects of CO_2 transfer in the pond and in the sluice tank are examined as well as the scaling potential of the systems. This section first discusses the simulation basis for these simulations, including the process model and input data. Then the results of the simulations are examined.

3.2.1 Simulation Basis

The process model used to simulate alternatives for ash sluicing operations is identical to that used for existing operations (see Appendix E). The ash flow rates and characteristics were the same as the values used for existing operations simulations. Sluice water rates were determined so that both bottom ash and fly ash were slurried at 10% solids.

Table 3-4 presents the input data that was used for the alternative sluicing operations. The makeup water for once-through sluicing of bottom ash and fly ash is 5.7 cycle cooling tower blowdown and for recirculating sluicing is 15 cycle blowdown.

3.2.2 Once-Through Ash Sluicing System

The simulation results for once-through ash sluicing at Bowen using cooling tower blowdown, with the towers operating at 5.7 cycles of concentration, as the sluice water are shown in Table 3-5. For this simulation, no transfer of carbon dioxide was allowed between the process liquor and the atmosphere at any point in the system. The effects of CO_2 mass transfer in the pond and in the sluice tank are examined in Section 3.2.4.

The relative saturation of calcium sulfate in the fly ash slurry indicates that gypsum scaling will not present any problem in the once-through ash sluice system. The calculated relative saturation of 0.66 is well below the critical scaling level of 1.3 - 1.4. However, scaling potential for both calcium carbonate and magnesium hydroxide is noted in the fly ash slurry. The calculated values for relative saturation of $CaCO_3$

TABLE 3-4. BOWEN ALTERNATIVE ASH SLUICING INPUT DATA

	Once-Through	Recirculating
Flows (Total Plant)		
Fly Ash, kg/min	1554	1554
(lb/min)	(3430)	(3430)
Fly Ash Sluice Maekup, ℓ/sec	234	94.6
(GPM)	(3700)	(1500)
Fly Ash Sluice Recycle, ℓ/sec	0	140.4
(GPM)	(0)	(2200)
Bottom Ash, kg/min	515	515
(lb/min)	(1135)	(1135)
Bottom Ash Sluice Makeup, ℓ/sec	77	0
(GPM)	(1220)	(0)
Bottom Ash Sluice Recycle, ℓ/sec	0	77
(GPM)	(0)	(1220)
Makeup Water Composition, mg/l*		
Calcium	34.3	90.2
Magnesium	9.7	25.5
Sodium	7.9	20.7
Chloride	12.2	32.0
Carbonates (as $CO_3^=$)	39.2	20.9
Sulfates (as $SO_4^=$)	69.7	249
Nitrates (as NO_3^-)	24.8	65.0
Pond Deposits, wt % solids	40	40
Soluble Ash Species (fly ash), wt %		
CaO	0.33	0.33
MgO	0.001	0.001
Na_2O	0.08	0.08
$CaSO_4$	1.25	1.25

*Once-through sluicing makeup water is 5.7 cycle cooling tower blowdown. Recirculating sluicing makeup water is 15 cycle cooling tower blowdown.

TABLE 3-5. BOWEN ONCE-THROUGH ASH SLUICING AT 10% SOLIDS*

	Makeup Sluice Water**	Fly Ash Slurry	Ash Pond Overflow
Flow, ℓ/sec	310	234	255
(GPM)	(4920)	(3700)	(4050)
Composition, mg/ℓ			
Calcium	34.3	712	520
Magnesium	9.7	10.5	.03
Sodium	7.9	74.5	58.3
Chloride	12.2	12.2	12.4
Carbonates (as $CO_3^=$)	39.2	39.2	0.7
Sulfates (as $SO_4^=$)	69.7	1060	817
Nitrates (as NO_3^-)	24.8	24.8	25.2
Temperature, °C	46.7	46.7	21.1
(°F)	(116)	(116)	(70)
pH	8.0	11.4	12.0
Relative Saturations***			
$CaCO_3$	0.98	127	1.0
$Mg(OH)_2$	4.7×10^{-4}	547	1.0
$CaSO_4 \cdot 2H_2O$	0.012	0.66	0.55

*No CO_2 transfer in the system.

**5.7 cycle cooling tower blowdown.

***Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$, about 2.5 for $CaCO_3$, and about 3.4 for $Mg(OH)_2$ (see Appendix C).

and $Mg(OH)_2$ are far in excess of the respective critical values of 2.5 and 3.4 (Appendix C).

One possible solution to the precipitation of calcium carbonate and magnesium hydroxide as scale in the sluice line is to install a reaction tank prior to the sluice line, whereby a significant portion of the solids may be formed in the tank as opposed to the line. One method to aid fly ash-sluice water mixing and precipitation of solids in the fly ash slurry tanks is to utilize two smaller tanks as opposed to one large tank to avoid channeling of streams in the slurry tank. Although the tank may be designed to minimize fouling in the slurry line, there is a high probability that some scaling of $CaCO_3$ and $Mg(OH)_2$ will occur and eventually foul the line.

A potential remedy to this situation is to periodically flush the line with a low pH water stream. Flush water in the pH range of 6 to 7 should be adequate to remove solid $CaCO_3$ and $Mg(OH)_2$ since they easily dissociate in this pH range. A possible source of flush water is acidified cooling tower blowdown. Frequent flushing of the fly ash slurry line with low pH water should maintain the line free of solid $CaCO_3$ and $Mg(OH)_2$. However, pilot or bench scale studies should be performed prior to implementing this alternative to accurately size the reaction tank and determine the quantity and frequency of flush water required or if other measures are necessary.

3.2.3 Recirculating Ash Sluicing System

The simulation results for a recirculating ash sluicing system at Bowen using cooling tower blowdown, with the towers operating at 15.0 cycles, as the makeup sluice water are shown in Table 3-6. As with the simulation discussed in the previous section, no CO_2 transfer between the atmosphere and the process liquor was allowed at any point in the system. The effects of CO_2 mass transfer will be discussed in Section 3.2.4.

The degree of recycle achievable in the ash sluicing system will depend upon the $CaSO_4 \cdot 2H_2O$ relative saturation since gypsum scale is of greater concern than that of $CaCO_3$ or $Mg(OH)_2$. Gypsum scale is very difficult to remove from process vessels and equipment once it is formed but $CaCO_3$ and $Mg(OH)_2$ scale most likely can be dissolved by acid washing.

TABLE 3-6. BOWEN RECIRCULATING ASH SLUICING*

	Makeup** Sluice Water	Pond Recycle	Fly Ash Slurry	Ash Pond Overflow
Flow, ℓ/sec	93.3	138.9	232.2	40.9
(GPM)	(1480)	(2200)	(3680)	(650)
Composition, mg/ℓ				
Calcium	90.2	1170	1410	1170
Magnesium	25.5	--	11.0	--
Sodium	20.7	187.6	187	187.6
Chloride	32.0	32.8	32.6	32.8
Carbonates (as $CO_3^=$)	20.9	0.7	8.9	0.7
Sulfates (as $SO_4^=$)	250	1280	1850	1280
Nitrates (as NO_3^-)	65.0	66.6	66.2	66.6
Temperature, °C	46.7	21.1	46.7	21.1
(°F)	(116)	(70)	(116)	(70)
pH	7.9	12.5	11.7	12.5
Relative Saturations***				
$CaCO_3$	0.79	1.0	29.3	1.0
$Mg(OH)_2$	6.3×10^{-4}	1.0	1458	1.0
$CaSO_4 \cdot 2H_2O$	0.067	1.0	1.28	1.0

*No CO_2 transfer allowed, gypsum precipitation in pond allowed, 60% of sluice water recycled.

**15-cycle cooling tower blowdown.

***Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$, about 2.5 for $CaCO_3$, and about 3.4 for $Mg(OH)_2$ (see Appendix C).

The amount of ash pond liquor recycled to the sluice system should be the maximum amount possible without exceeding the critical scaling level of 1.3 - 1.4 for the relative saturation of $CaSO_4 \cdot 2H_2O$ in the fly ash sluice system. Exceeding this critical value could cause plugging of the slurry line. Maximizing the amount of recycle in the overall system will minimize the quantity of ash pond effluent to be treated and therefore minimize the cost of treatment. These simulations were performed for the exclusive use of pond water for sluicing bottom ash and 60% recycle in the fly ash system.

The level of supersaturation in the pond recycle water with respect to gypsum will affect the scaling potential in the slurry line and should be considered. The case shown in Table 3-6 assumes that the gypsum relative saturation of the pond recycle is 1.0. A discussion of the effects of supersaturation in the pond recycle liquor is given in Section 3.2.5.

The relative saturation of gypsum in the fly ash slurry reaches 1.28 for the recirculating configuration as shown in Table 3-6, indicating an approach to the critical range for scaling. This level of recycle in the ash sluice system therefore represents the maximum operating limit (based on $CaSO_4 \cdot 2H_2O$) without chemical treatment, since the critical range for scale formation is 1.3 - 1.4. For this case about 60% of the fly ash sluice water is recycled from the pond.

As in the once-through sluicing case, the relative saturations of calcium carbonate and magnesium hydroxide are significantly above the critical levels. The values shown in Table 3-6 are 29.3 for $CaCO_3$ and 1,458. for $Mg(OH)_2$, whereas the respective critical values are 2.5 and 3.4. Again, $CaCO_3$ and $Mg(OH)_2$ scale formation in the slurry line may be reduced by installing a reaction tank prior to the sluice line. Sizing this tank is critical to the successful operation of this ash sluicing configuration. Additional data should be taken on a pilot scale so that the reaction tanks may be accurately sized before implementing this alternative. Flush water may possibly be used (at pH 6-7) to clean any $CaCO_3$ or $Mg(OH)_2$ solid deposits at periodic intervals, as suggested for once-through sluicing. Pilot or bench scale testing to determine the level of acid washing that is sufficient to prevent the line from plugging should be conducted before this alternative is implemented.

The ash pond overflow is reduced from 255 ℓ/sec (4050 GPM) in the once-through simulation case to 40.9 ℓ/sec (650 GPM) for this case. Treatment of this stream to achieve zero discharge could be accomplished by a combination softening/reverse osmosis/brine concentration treatment unit. A portion of the clean water resulting from treatment (50%) could be recycled to the system as boiler makeup water. In the event SO_2 scrubbers are installed at Bowen, the ash pond overflow could be used as makeup water to the scrubbers to utilize the available ash alkalinity.

3.2.4 Effects of Carbon Dioxide Mass Transfer

Five additional cases were studied to determine the effects on the operation of the ash sluicing system of carbon dioxide mass transfer between the process liquor and the atmosphere. The results from these additional cases along with the two base cases previously discussed are shown in Table 3-7.

Two additional cases for once-through sluicing operation were run: 1) allowing the process liquor in the pond to be in equilibrium with the atmosphere with respect to CO_2 and 2) allowing CO_2 equilibrium with the atmosphere in the sluice tank.

Allowing CO_2 equilibrium in the ash pond has no effect on the fly ash slurry, but reduces the ash pond overflow pH to 8.0 from the value of 12.0 for the base case. Carbon dioxide equilibration in the sluice tank indicates an increase in scale potential for $CaCO_3$ but completely eliminates $Mg(OH)_2$ scale potential. The decrease in the pH of the ash slurry causing a carbonate shift away from the carbonate ion ($CO_3^=$) towards bicarbonate (HCO_3^-), is more than offset by the increase in total CO_2 in the liquid phase, resulting in an increase in $CaCO_3$ scaling potential (relative saturation changed from 126.7 for the base case to 965.6).

The drop in pH from 11.4 to 9.1 for the ash slurry is the reason for the $Mg(OH)_2$ relative saturation decrease from 547.4 to 0.035. Gypsum relative saturation decreased slightly between the base case and the additional case. The net result is that achieving CO_2 equilibrium between the atmosphere and the process liquor in the tank is beneficial from the standpoint of reducing $Mg(OH)_2$ scale potential. In actual practice it is not likely that equilibrium would be completely achieved in the tank but the relatively high values of pH (11.4) enhance

TABLE 3-7. EFFECTS OF CO_2 TRANSFER ON BOWEN ASH SLUICING OPERATIONS

	Once-Through Sluicing			Recirculating Sluicing			
	Base Case	Case 2	Case 3	Base Case	Case 2	Case 3	Case 4
CO_2 Equilibrium in Pond	No	Yes	--	No	Yes	No	Yes
CO_2 Equilibrium in Tank	No	No	Yes	No	No	Yes	Yes
Fly Ash Slurry Relative Saturations*							
$CaCO_3$	126.7	126.7	956.6	29.3	89.1	2,766.	956.6
$CaSO_4 \cdot 2H_2O$	0.66	0.66	0.62	1.28	1.35	1.19	1.28
$Mg(OH)_2$	547.4	547.4	0.035	1,458.	1,198.	0.051	0.062
pH	11.4	11.4	9.1	11.7	11.3	9.3	9.1
Pond Overflow pH	12.0	8.0	--	12.5	7.9	--	--

*Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$, about 2.5 for $CaCO_3$, and about 3.4 for $Mg(OH)_2$ (see Appendix C).

the sorption of CO_2 along with agitation of the liquid phase. However, the short residence time in the sluice tank would minimize the CO_2 transfer (see Appendix L).

Three additional cases were run for the recirculating ash sluicing system: 1) CO_2 equilibrium in the pond only, 2) CO_2 equilibrium in the tank only, and 3) CO_2 equilibrium in both the tank and the pond. Case 2 in Table 3-7 shows that CO_2 equilibration between the atmosphere and the liquor in the pond increases the $CaCO_3$ scale potential (relative saturation increased from 29.3 to 89.1) but decreases the $Mg(OH)_2$ scale potential (relative saturation decreased from 1,458. to 1,198.) in the fly ash slurry. The calcium sulfate relative saturation increased from 1.28 to 1.35.

Case 3, representing CO_2 equilibrium with the atmosphere in the sluice tank but no CO_2 transfer in the pond, indicates that the $CaCO_3$ scale potential is greatly increased, but the $CaSO_4 \cdot 2H_2O$ and $Mg(OH)_2$ relative saturations are decreased to values below the critical scaling levels. The gypsum relative saturation decreased from 1.28 in the base case to 1.19 due to the increased calcium associated with carbonate ions in solution, which lowers the calcium ion activity. The $Mg(OH)_2$ relative saturation decrease from 1,458. in the base case to 0.051 is due to the decrease in the pH of the ash slurry from 11.7 to 9.3.

The last case which represents operation where CO_2 equilibrium is achieved both in the pond and in the sluice tank showed an increase in $CaCO_3$ scale potential, no change in gypsum relative saturation, and elimination of $Mg(OH)_2$ scale potential.

Since gypsum scale is the most important factor to control in the system due to the difficulty of removing the scale, Case 3 represents the most favorable case. Although complete CO_2 equilibration in the tank and no CO_2 transfer in the pond may not be achieved in actual practice, the system may be operated to maximize the CO_2 transfer in the tank and minimize CO_2 transfer in the pond. The transfer in the pond may be minimized by taking the recycle liquor from a point near the discharge of the slurry, such that enough residence time has been allowed for solids settling. Although CO_2 transfer has not been quantified in this study, pilot scale studies to determine the optimum ash sluicing recycle configuration may provide data to allow a more accurate account of the level of CO_2 transfer in actual operations.

3.2.5 Effect of $CaSO_4 \cdot 2H_2O$ Supersaturation in the Pond Recycle Water

If the pond recycle water in a recirculating ash sluice system at Bowen remains supersaturated with respect to gypsum, scaling may occur in the fly ash sluice line. The degree of supersaturation in the pond recycle water cannot be accurately quantified but will depend on the degree of turbulence in the pond and on the residence time in the pond. The greater the degree of mixing in the pond due to thermal gradients or wind turbulence, the more desupersaturated the liquor will become. Longer residence times will also encourage precipitation.

However, the lack of $CaSO_4 \cdot 2H_2O$ crystals in the pond will discourage any precipitation and therefore, limit the degree of desupersaturation. Since ponds are generally not very well mixed, the pond will most likely remain supersaturated with respect to gypsum as long as no chemical treatment is used, and scaling may occur. Pilot or bench scale testing may provide information to more accurately determine the degree of desupersaturation.

The magnitude of chemical treatment to remove calcium from the system was calculated using the chemical equilibrium program. Sodium carbonate softening of 80% of the pond recycle water is necessary assuming that no $CaSO_4 \cdot 2H_2O$ precipitation occurs in the pond and that all of the cooling tower blowdown (towers operating at 15 cycles) is used as makeup water to the fly ash system. Bottom ash was assumed to be sluiced exclusively with pond water.

Treatment of 80% of the recycle liquor corresponds to removing 2.7 gmole/sec calcium from a 206 ℓ/sec (3270 GPM) stream. Treatment inefficiencies were taken into account by assuming that the treated stream contains 50 mg/ℓ calcium. The equilibrium value with stoichiometric addition of Na_2CO_3 is 22.4 mg/ℓ as calculated by the chemical equilibrium program.

3.2.6 Summary of Ash Sluicing Operations

Two sluicing configurations were studied: once-through sluicing of both bottom ash and fly ash at 10% solids and recirculating sluicing with 60% recycle in the fly ash system and 100% recycle in the bottom ash system. The once-through calculations show that no gypsum scale potential is present but $CaCO_3$ and $Mg(OH)_2$ are highly supersaturated.

The recirculating system using 15 cycle cooling tower blowdown as makeup requires softening 80% of the pond recycle assuming the pond will not desupersaturate with respect to gypsum. A pond overflow of 41.0 ℓ/sec (650 GPM) is produced from the recirculating system as opposed to 255 ℓ/sec (4050 GPM) from the once-through system.

The net result of the studies concerning CO_2 transfer indicate that the level of CO_2 transfer has only a small effect on gypsum scale potential but does alter the $CaCO_3$ and $Mg(OH)_2$ relative saturations. In general CO_2 absorption raises the $CaCO_3$ relative saturation and lowers the $Mg(OH)_2$ relative saturation.

3.3 Conclusions

From the results of the cooling tower and ash sluice system simulations discussed in the previous sections, two alternatives for reducing plant discharges are considered technically feasible. These are:

1) Cooling tower operation at 5.7 cycles with acid treatment and once-through ash sluicing with discharge of ash pond overflow after pH adjustment, and

2) Cooling tower operation at 15.0 cycles with acid treatment and recirculating ash sluice (Na_2CO_3 softening of 80% of pond recycle) with either discharge of the ash pond overflow after pH adjustment or treatment of the overflow with a softening/reverse osmosis/brine concentration unit and recycle of the clean water as boiler makeup and cooling tower makeup.

The first alternative will require the addition of acid treatment in the cooling towers and reaction tanks prior to the fly ash sluice line to minimize $CaCO_3$ and $Mg(OH)_2$ scale formation in the line. Adjustment of the pH of the ash pond overflow may be required, depending on the amount of carbon dioxide mass transfer occurring in the pond. The calculated pH for equilibrium with respect to CO_2 between the pond liquor and the atmosphere is 8.0 whereas the value for no CO_2 transfer is 12.0. This alternative would not allow Bowen to achieve zero-discharge without expensive treatment of the ash pond overflow (255 ℓ/sec or 4050 GPM), but would reduce the plant makeup water and discharge rates significantly. The existing ash pond overflow rate for Bowen is about 1600 ℓ/sec (25,000 GPM) and could be reduced to about 255 ℓ/sec (4050 GPM) by this alternative.

Treatment of the ash pond overflow by the lime-soda ash process would reduce the calcium, magnesium, and silica levels but sulfate concentrations would reach a high enough level for gypsum scaling to occur. Effective treatment could be achieved by softening/reverse osmosis/brine concentration but only at a severe economic penalty due to the magnitude of the stream flow.

If in the future, SO_2 scrubbers are installed at Bowen, the ash pond overflow could be used as makeup water to the scrubbing system to make use of the available alkalinity from the ash. However, this study does not include the addition of scrubbers at Bowen, but considers only the cooling and ash handling systems.

The second alternative will require the addition of acid treatment in the cooling towers and reaction tanks in the fly ash sluice system as in the first alternative. In addition, recycle lines and pumps to return a portion of the ash pond liquor for sluicing and sodium carbonate softening of 80% of the pond recycle water are required. Zero-discharge may be achieved with this alternative by treatment of the ash pond overflow by a softening/reverse osmosis/brine concentration unit and returning the cleaned water to the boilers' and cooling towers' makeup systems. Discharge of the ash pond overflow may require pH adjustment as in the first alternative depending on the level of CO_2 transfer in the pond. Also, silica removal may be required at 15 cycles of concentration in the cooling tower system.

It should be emphasized here that neither alternative should be implemented before more information is gathered from a bench or pilot scale test program to determine 1) the actual size of reaction tank required in the sluice system, 2) the quantity and frequency of acid wash water required to minimize $CaCO_3$ and $Mg(OH)_2$ scale formation, 3) the level of gypsum desupersaturation in the pond, and 4) the scaling control limits for silica solids.

An economic analysis based on rough cost estimates for these two alternatives is presented in the next section.

4.0 ECONOMICS

This section provides rough cost estimations for implementing each of the technically feasible alternatives discussed in Section 3.0. Both rough capital costs and operating costs are presented. The assumptions used in calculating these costs are briefly outlined. It is emphasized that these values are only rough estimates for comparative purposes.

A capital cost summary for the two technically feasible alternatives is presented in Table 4-1. The fly ash slurry tanks were sized based on a five minute residence time of the slurry to allow most of the ash soluble species to be leached in the tank. These tanks were assumed to be general storage tanks equipped with wear liners for costing purposes. One tank was used for the fly ash slurry from each unit and was assumed to have one agitator to keep the slurry well mixed.

Pond overflow recycle pumps and piping were sized based on the flows calculated in the simulations discussed in Section 3.0. Twelve-inch carbon steel buried pipe with average fittings, flanges, shop coating, and wrapping was assumed for pond return lines to the fly ash systems. Eight and ten-inch pipe was assumed for the bottom ash systems. A labor to material ratio of 0.8 was used to determine installation costs. Engineering costs (direct and indirect) were assumed to be 7.2% of the combined labor and material cost (GU-075).

Cast steel pumps with electric motor drivers were used for all streams. A labor to material ratio of 0.36 was used for installation costs. Engineering was assumed to be 10% of the combined labor and material cost (GU-075). All pump and piping costs were upgraded from 1970 dollars to 1976 dollars using a factor of 1.56 (based on Chemical Engineering Index).

Since both alternatives involve sluicing the ash at 10 wt% solids, the tank and agitator costs are identical. The difference in capital cost is due to the installation of pumps and piping for recycling a portion of the ash pond liquor and Na_2CO_3 softening of the pond recycle liquor for alternative two.

A summary of the operating costs for the two alternatives is shown in Table 4-2. Four major breakdowns are shown: acid treatment, power consumption, softening, and capital cost

TABLE 4-1. CAPITAL COSTS* FOR WATER RECYCLE/REUSE ALTERNATIVES AT BOWEN

	Alternative One (Once-through ash sluice)	Alternative Two (Recirculating ash sluice)
Fly Ash Slurry Tanks**	61,000	61,000
Agitators	21,000	21,000
Pond Overflow Recycle Pumps	--	105,000
Pond Overflow Recycle Piping	--	507,000
Sodium Carbonate Softening	--	300,000
Contingency (20%)	16,000	199,000
Contractual Fees (3%)	2,000	30,000
TOTAL	100,000	1,223,000

*1976 dollars

**Includes wear liner and agitator supports

***$91.7/GPM (1976 dollars) or $75/GPM (1974 dollars)

References: GU-075, MC-136, NE-107

TABLE 4-2. OPERATING COSTS[1] FOR WATER RECYCLE/REUSE ALTERNATIVES AT BOWEN

	Alternative One	Alternative Two
Cooling Tower Acid Treatment[2]	35,800	45,400
Power Consumption[3]		
Agitators	2,100	2,100
Recycle Pumps	--	51,300
Softening Chemicals[4]	--	120,000
Capital Charges[5]	15,000	183,000
TOTAL	52,900	401,800
(mils/kw-hr)	(.002)	(.018)

[1] 1976 dollars/yr based on 80% load factor
[2] \$60/ton for sulfuric acid
[3] 2¢/kw-hr
[4] \$69/10^6 gal (NE-107)
[5] 15% per year based on 30-year lifetime

amortization. The acid treatment costs were based on $60/ton for sulfuric acid and were calculated based on the simulation results in Section 3.0. Operating the towers at 15.0 cycles of concentration (alternative 2) will require 27% more acid than operation at 5.7 cycles (alternative 1). The difference in power consumption for the two alternatives is due to the recycle pumps employed in the second alternative. A cost of 2¢/kw-hr was used to determine power costs.

The results shown in Tables 4-1 and 4-2 indicate that the first alternative is significantly less expensive than the second. However, to achieve zero-discharge by eliminating the ash pond overflow discharge is not practical for the first alternative (once-through ash sluicing) due to the magnitude of the flow (255 ℓ/sec or 4,050 GPM).

Additional capital and operating costs for treating the ash pond overflow (41 ℓ/sec or 650 GPM) from the second alternative are presented in Table 4-3. The overflow can be treated by a combination of softening, reverse osmosis, and brine concentration and the clean water recycled to the plant boiler makeup system. The additional capital cost is about $5.16 million giving a total capital cost of about $6.38 million for achieving zero-discharge with a recirculating ash sluice system. The additional operating costs total approximately $1,333,000/yr to give a total operating cost of about $1.74 million/yr for achieving zero discharge.

TABLE 4-3. CAPITAL AND OPERATING COSTS FOR ELIMINATING ASH POND OVERFLOW AT BOWEN

	Capital Cost[1]	Operating Cost[2]
Softening/Reverse Osmosis/ Brine Concentrator[3]	5,040,000	546,000
Additional Pump	22,000	13,000
Additional Piping	95,000	--
Additional Capital Charges[4]	--	774,000
Total Additional Costs	5,157,000	1,333,000
Costs from Tables 4-1, 4-2 (to nearest $1000)	1,223,000	402,000
TOTAL (mils/kw-hr)	6,380,000	1,735,000 (.078)

[1] 1976 dollars

[2] 1976 dollars per year

[3] capital cost = $7,750/GPM feed (LE-239)
operating costs = $2/1,000 gal not including capital cost amortization

[4] 15% per year for 30 year lifetime

Appendix H. Recycle/Reuse Options at Comanche (Public Service of Colorado)

1.0 INTRODUCTION

This appendix describes the analysis of the water system at the Public Service of Colorado's (PSC) Comanche Plant. The work was done under EPA Contract No. 68-03-2339, Water Recycle/Reuse Alternatives in Coal-Fired Steam-Electric Power Plants. In this section a summary of the important results is presented. Comanche was chosen along with four other plants for evaluation of technical and economic feasibility of various water recycle/reuse options. The major water systems at the two-unit, 700 Mw Comanche plant are the cooling tower and bottom ash sluicing systems. Fly ash is disposed of in a dry form.

The results of the existing operations simulations for the Comanche cooling system compare well with the sample data obtained at the plant. The calculated $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ relative saturations in the recirculating cooling water (8.2×10^{-4} and 0.252, respectively) indicate that the cycles of concentration may be significantly increased without forming calcium carbonate or calcium sulfate (gypsum) scale. However, the high level of the silica concentration in the makeup water may require some form of silica removal, such as lime-soda ash or magnesium bicarbonate treatment, in order to prevent silica scaling at higher cycles of concentration. Pilot or bench-scale studies to more accurately quantify silica scaling potentials are recommended before increasing the cycles of concentrations in the Comanche cooling system.

Cooling system simulations were carried out to determine the effects of operating at increased cycles of concentration in the towers. In addition, system sensitivity to composition changes in the makeup water were investigated by simulations using a makeup water with twice the sulfate concentration found in the sample data.

Table 1-1 presents a summary of the three alternatives which were examined for Comanche. It should be noted here that this analysis was performed to study general water recycle/reuse alternatives. Actual implementation of any of the alternatives would require a more extensive investigation of process parameter variability. More water quality data would be required along with additional studies to fully characterize the ash reactivity variations as a function of time. The first one involved using cooling system blowdown from the towers designed to operate at five cycles of concentration to sluice both fly ash and bottom ash on a once-through basis. The effects of CO_2 mass transfer

TABLE 1-1. SUMMARY OF WATER RECYCLE/REUSE OPTIONS AT COMANCHE

	Existing Conditions	Alternative One	Alternative Two	Alternative Three
Cooling Tower Makeup Source	Softened River Water	Softened River Water	Softened River Water	Softened River Water
Cycles of Concentration in Cooling Towers	5.0	5.0	7.6	8.4
Cooling System Treatment	(Sulfuric acid and zinc polyphosphate used for all conditions)			
Fly Ash Disposal Method Type, % solids	Dry	Wet, 10%	Wet, 10%	Dry
Bottom Ash Disposal Method Type, % solids	Wet, 1%	Wet, 4%	Wet, 4%	Wet, 1%
Recycle in Fly Ash System, %	---	0	10%	---
Recycle in Bottom Ash System, %	0	0	100%	76%[3]
Treatment in Ash Systems	None	None	Brine Concentration of Makeup (50%)	None
Plant Makeup Requirements ℓ/sec (GPM)	590 (9350)	520 (8250)	455 (7210)	450 (7120)
Plant Discharge ℓ/sec (GPM)	156 (2470)	65.4 (1040)	28.8 (460)	30.2 (480)
Costs[1]				
Capital Investment, 1976 $	---	342,000	3,662,000	222,000
Operating Expenditures, 1976 $/yr[2] (mils/kW-hr)	---	90,000 (0.02)	863,000 (0.18)	38,000 (0.008)
Additional Cost to Treat Pond Overflow for Zero Discharge				
Capital, 1976 $	---	8,280,000	3,706,000	3,883,000
Operating, 1976 $/yr[2]	---	2,136,000	944,000	989,000
(mils/kW-hr)	---	(0.43)	(0.19)	(0.20)
Total Cost for Zero Discharge				
Capital, 1976 $	---	8,622,000	7,368,000	4,105,000
Operating, 1976 $/yr[2]	---	2,226,000	1,807,000	1,027,000
(mils/kW-hr)	---	(0.45)	(0.37)	(0.21)

---

[1] These rough cost estimates were made to compare technically feasible options and do not include a "difficulty to retrofit" factor

[2] Includes capital amortization at 15% per year.

[3] About 813 GPM of pond water is recycled in this alternative and represents about 76% of the total sluice water required for 1% solids in the bottom ash slurry.

in the ash pond and the sluice tank were examined for this system. No gypsum scale potential was identified in any of the once-through sluicing cases, but potential scaling of $CaCO_3$ and $Mg(OH)_2$ was present.

It is possible that the fly ash slurry line can be kept free of plugging by the addition of a fly ash slurry reaction tank and by frequent flushing with water of pH 6 to 7. Pilot or bench scale studies are recommended to size the reaction tank and determine the quantity of wash water required or if other measures are required before implementing fly ash sluicing at Comanche. This alternative will result in an ash pond overflow of about 32.7 ℓ/sec (518 GPM) for each unit as compared to the existing configuration bottom ash pond overflow rate of about 78 ℓ/sec (1230 GPM) per unit.

The second alternative involves sluicing the fly ash at about 10 wt.% solids using 90% cooling tower blowdown and 10% ash pond recycle water. Bottom ash is sluiced at about 4 wt.% solids using only pond recycle water. Gypsum relative saturations in the fly ash sluice line were calculated to be 1.54 - 1.74 depending on the level of CO_2 transfer in the pond. This range exceeds the critical relative saturation range for scaling of $CaSO_4 \cdot 2H_2O$ of 1.3-1.4. Therefore, some form of treatment would be required such as brine concentration of a portion of the tower blowdown. Lime treatment of the blowdown for calcium removal was found to be insufficient for scale prevention due to the sulfate concentrations in the system. Desupersaturation of gypsum in the ash pond will also not prevent scaling since only a small portion (10%) of the ash pond liquor is recycled to the fly ash system.

As with the once-through simulations, potential for $CaCO_3$ and $Mg(OH)_2$ scaling was identified. But, as before, this possibly can be minimized by installing a reaction tank prior to the sluice line and by flushing the line frequently with a pH 6-7 water stream. Again, further testing is suggested. This alternative will produce an ash pond overflow of about 14.4 ℓ/sec (230 GPM) for each unit.

The third alternative is to continue to dispose of fly ash in a dry form and sluice the bottom ash on a recirculating basis using cooling tower blowdown and pond recycle with the towers operating at 8.4 cycles of concentration. This will provide 16.0 ℓ/sec (260 GPM) of cooling tower blowdown per unit and will not alter the boiler refractory cooling systems. For this alternative about 15.1 ℓ/sec (240 GPM) of ash pond overflow per unit will be obtained. This water may be discharged or recycled to the boiler and cooling tower makeup systems after appropriate treatment.

Rough cost estimates were made for the once-through sluice system and the recirculating system using cooling tower blowdown to sluice fly ash with 50% of the blowdown treated by brine concentration. Operating the cooling system at 5 cycles of concentration and sluicing the fly ash and bottom ash on a once-through basis is the less expensive alternative ($342,000 for capital cost and about $90,000/yr operating cost, including capital amortization at 15% per year). The third alternative is the least expensive with $222,000 capital costs and $38,000/yr operating costs.

In order to reduce the ash pond overflow to 14.4 ℓ/sec (229 GPM) for each unit by operating the cooling systems at 7.6 cycles of concentration with the cooling system blowdown as sluicing makeup, the entire plant ash sluice system will require an initial capital cost of about $3.7 million and an operating cost of about $863,000/yr, including capital amortization at 15% per year. These costs do not include the possible necessity of silica removal.

If zero discharge of ash pond overflow is desired, the once-through system becomes more expensive due to the greater amount of ash pond overflow to be treated. A softening/reverse osmosis/brine concentration system to eliminate ash pond overflow would require an additional operating cost of approximately $2,136,000/yr. The total overall costs would be about $8,622,000 for capital costs and $2,226,000/yr for operating costs (including capital cost amortization at 15% per year).

The additional costs for obtaining zero discharge with the recirculating system would be about $3.7 million for capital costs and $944,000/yr for operating costs, giving total overall costs of about $7.4 million for capital costs and $1.8 million/yr for operating costs including capital amortization at 15% per year.

The costs associated with achieving zero discharge with dry fly ash disposal (third alternative) are about $4.1 million for capital costs and $1,027,000/yr for operating costs. These costs include brine concentration, additional piping, additional pumping costs, and capital amortization at 15% per year.

Detailed discussions of the existing operations simulations, the alternative simulations, and the rough cost estimates make up the main body of this appendix.

2.0 PLANT CHARACTERISTICS

The Public Service of Colorado Comanche generating station is a coal-fired system composed of two units, each having a 350 Mw capacity, and is located near Pueblo, Colorado. The coal burned at Comanche is about 7.3% ash and 0.4% sulfur with a heating value of about 8300 Btu/lb. The basic flow schemes are the same for both units as described in this section.

The Comanche cooling system uses wet cooling towers to discharge heat. The ash removal system consists of (1) wet sluicing for bottom ash, and (2) electrostatic precipitation and subsequent dry disposal for fly ash. The bottom ash slurry is sent to ash ponds for disposal.

These major features of the Comanche operation are discussed in detail in the following sections. The overall water balance will be described first followed by a more detailed description of the cooling and bottom ash sluicing systems. Then a brief description of the computer simulation model that was used to characterize the existing operations of the cooling system will be presented. A more detailed description of the models used can be found in Appendix E. The results of the existing operations simulations are compared to actual plant data and examined for potential water recycle/reuse alternatives.

2.1 Overall Water Balance

A flow schematic for the Comanche water system is given in Figure 2-1. Both the cooling system and the ash sluicing system are shown with the design flow rates and chemical analyses of the streams. The chemical analyses were performed on spot samples collected at Comanche. A detailed description of the sampling and analytical procedures used is presented in Appendix B.

Under existing operations the water input to the overall system is first taken from the Arkansas River and stored in a raw water reservoir. From here a small portion of the raw water (about 7 ℓ/sec or 105 GPM) is sent to the coal handling facilities to suppress dust generation. Another portion of the flow from the reservoir is sent to the ash removal system to sluice bottom ash into the ash ponds. The remainder of the raw water leaving the reservoir is sent to the Comanche lime treatment facility to reduce the calcium hardness. The lime sludge produced during the softening process is sent to a special ash

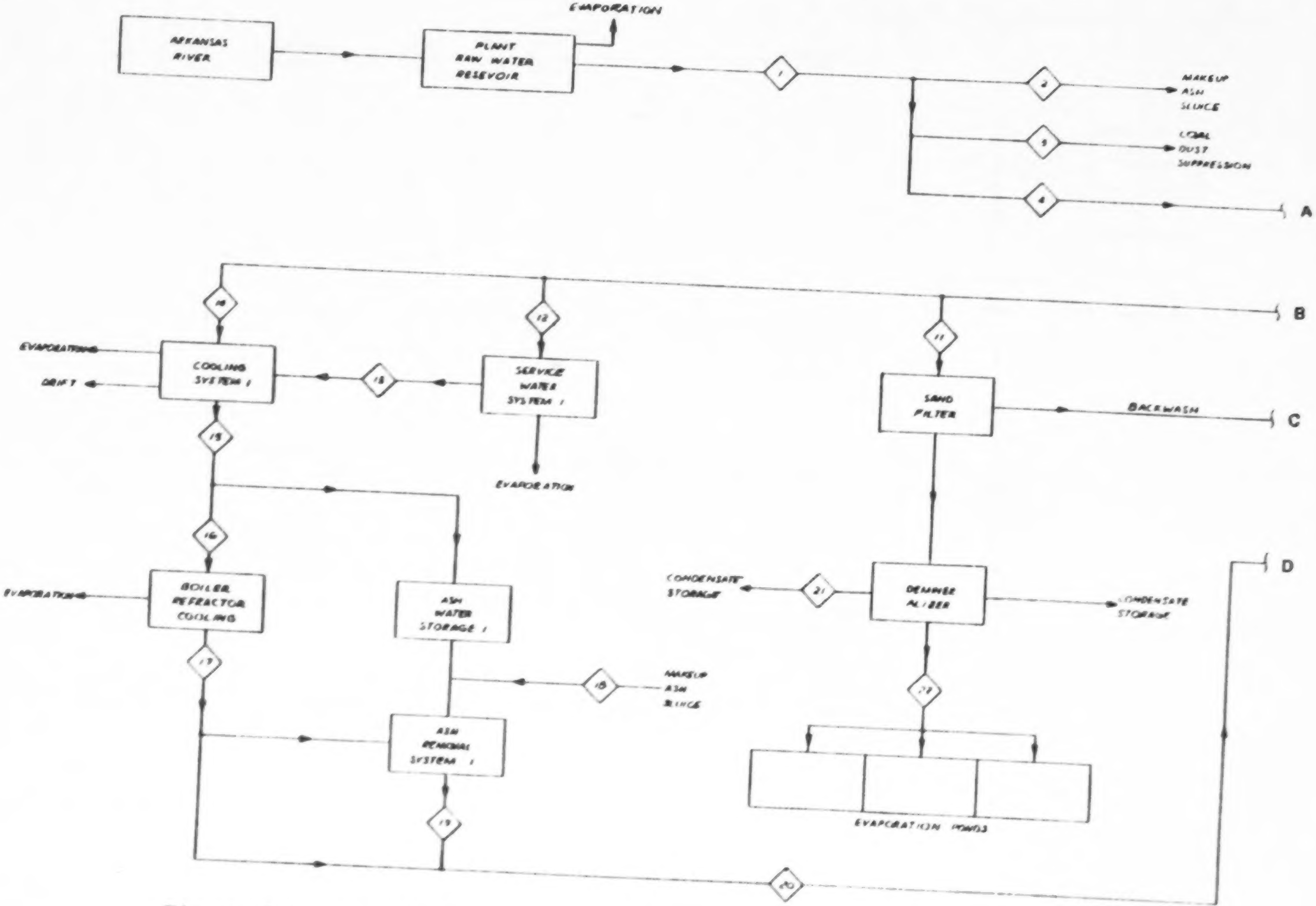


Figure 2-1. Public Service of Colorado Comanche Plant water balance.

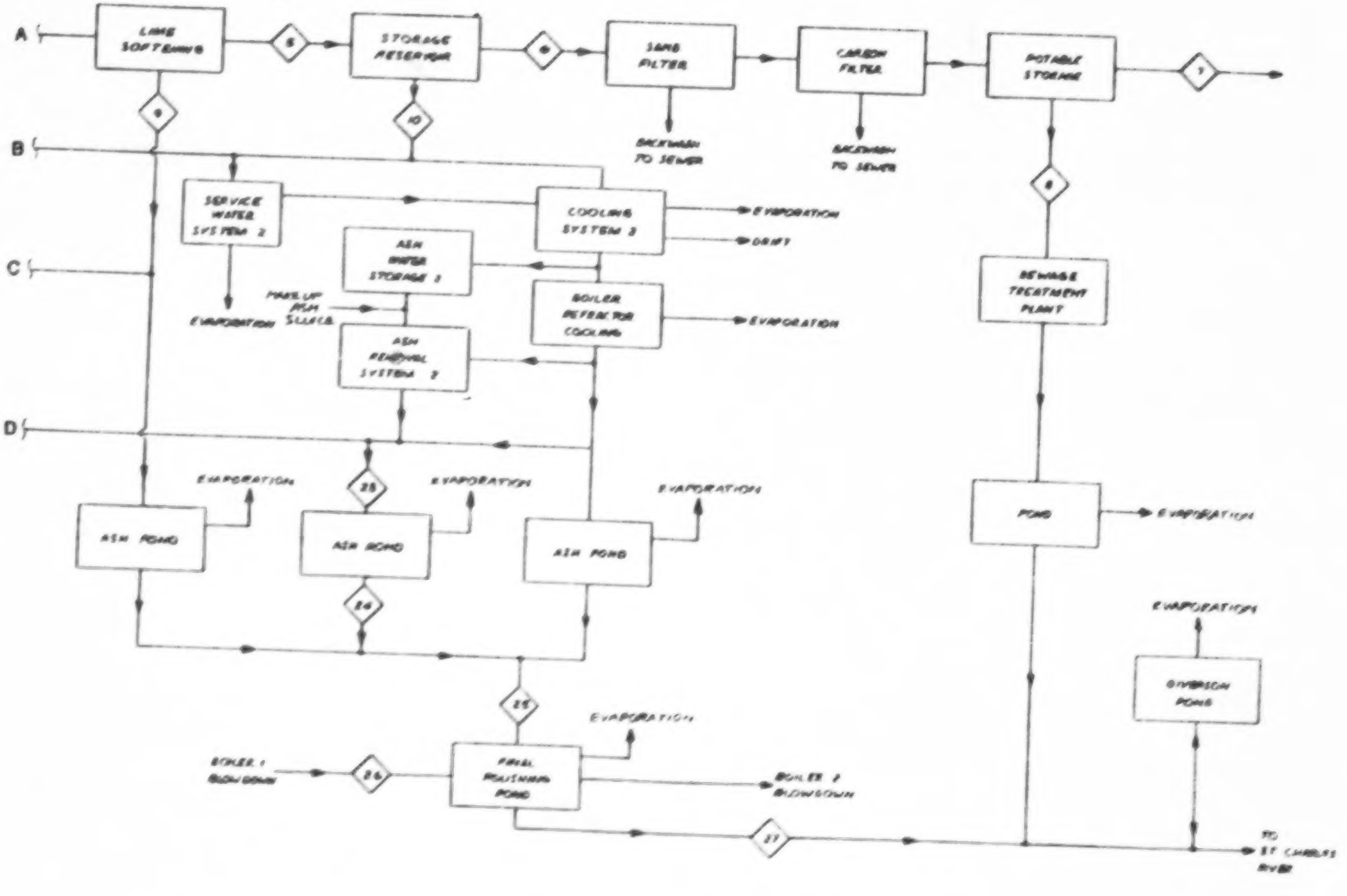


Figure 2-1. (Continued)

Stream Number			1	2	3	4	5	6	7	8	9
Stream Name			Plant Makeup	Makeup Ash Sluice	Coal Dust Suppression	Lime Softener Feed	Softened Water	Potable Makeup	Potable Water	Sewage Treatment Feed	Softening Wastes
Flow	Summer:	Metric English	590 ℓ/sec. 9,348 gpm	69 ℓ/sec. 1,100 gpm	7 ℓ/sec. 105 gpm	514 ℓ/sec. 8,143 gpm	510 ℓ/sec. 8,078 gpm	0.4 ℓ/sec. 6 gpm	0.2 ℓ/sec. 3 gpm	0.2 ℓ/sec. 3 gpm	4 ℓ/sec. 65 gpm
	Winter:	Metric English	488 ℓ/sec. 7,731 gpm	89 ℓ/sec. 1,410 gpm	7 ℓ/sec. 105 gpm	392 ℓ/sec. 6,216 gpm	389 ℓ/sec. 6,166 gpm	0.4 ℓ/sec. 6 gpm	0.2 ℓ/sec. 3 gpm	0.2 ℓ/sec. 3 gpm	3 ℓ/sec. 50 gpm
pH			8.55	8.55	8.55	8.55					
Calcium			53.4	53.4	53.4	53.4					
Magnesium			14.2	14.2	14.2	14.2					
Sodium			19	19	19	19					
Potassium			2.3	2.3	2.3	2.3					
Chloride			7	7	7	7					
Carbonate (as CO_3)			101	101	101	101					
Sulfate (as SO_4)			134	134	134	134					
Nitrate (as NO_3)			13	13	13	13					
Phosphates (as PO_4)			<0.1	<0.1	<0.1	<0.1					
Silicates (as SiO_2)			11	11	11	11					
Suspended Solids			<0.01	<0.01	<0.01	<0.01					
Dissolved Solids			345	345	345	345					

Figure 2-1. (Continued)

Stream Number		10	11	12	13	14	15	16	17	18
Stream Name		Softened Water	Boiler Makeup	Service Water	Service Water to Towers	Cooling Tower Makeup	Cooling Tower Blowdown	Boiler Cooling	Boiler Cooling	Makeup Ash Sluice
Flow	Summer: Metric English	509 ℓ/sec. 8,072 gpm	5 ℓ/sec. 76 gpm	11 ℓ/sec. 172 gpm	3.3 ℓ/sec. 52 gpm	241 ℓ/sec. 3,826 gpm	41 ℓ/sec. 655 gpm	16 ℓ/sec. 260 gpm	14 ℓ/sec. 225 gpm	35 ℓ/sec. 550 gpm
	Winter: Metric English	389 ℓ/sec. 6,160 gpm	5 ℓ/sec. 76 gpm	8 ℓ/sec. 132 gpm	2.7 ℓ/sec. 42 gpm	184 ℓ/sec. 2,910 gpm	32 ℓ/sec. 500 gpm	16 ℓ/sec. 260 gpm	14 ℓ/sec. 225 gpm	44 ℓ/sec. 705 gpm
pH						6.2	6.3	6.3		8.55
Calcium						36.5	205	205		53.4
Magnesium						10.2	65.5	65.5		14.2
Sodium						19	89	89		19
Potassium						1.7	13	13		2.3
Chloride						9	53	53		7
Carbonate (as CO_3)						6.0	2.7	2.7		101
Sulfate (as SO_4)						163	965	965		134
Nitrate (as NO_3)						9	16	16		13
Phosphates (as PO_4)						<0.1	3.5	3.5		<0.1
Silicates (as SiO_3)						54	280	280		11
Suspended Solids						<0.01	<0.01	<0.01		<0.01
Dissolved Solids						298	1,700	1,700		345

Figure 2-1. (Continued)

Stream Number		19	20	21	22	23	24	25	26	27
Stream Name		Bottom Ash Slurry	Bottom Ash Slurry	Clean Boiler Makeup	Demineralize Waste	Ash Pond Influent	Ash Pond Effluent	Polishing Pond Influent	Boiler Blowdown	Polishing Pond Effluent
Flow	Summer: Metric English	63 ℓ/sec. 1,000 gpm	74 ℓ/sec. 1,170 gpm	2 ℓ/sec. 35 gpm	0.4 ℓ/sec. 6 gpm	74 ℓ/sec. 1,170 gpm	74 ℓ/sec. 1,170 gpm	152 ℓ/sec. 2,405 gpm	2 ℓ/sec. 30 gpm	156 ℓ/sec. 2,465 gpm
	Winter: Metric English	63 ℓ/sec. 1,000 gpm	74 ℓ/sec. 1,170 gpm	2 ℓ/sec. 35 gpm	0.4 ℓ/sec. 6 gpm	74 ℓ/sec. 1,170 gpm	74 ℓ/sec. 1,170 gpm	151 ℓ/sec. 2,390 gpm	2 ℓ/sec. 30 gpm	155 ℓ/sec. 2,450 gpm
pH						7.45	7.25			7.7
Calcium						115	105			149
Magnesium						18.3	24.4			33.4
Sodium						29	44			39
Potassium						3.6	5.8			6.9
Chloride						12	16			27
Carbonate (as CO$_3$)						111	80			67
Sulfate (as SO$_4$)						260	355			528
Nitrate (as NO$_3$)						19	17			13
Phosphates (as PO$_4$)						0.1	0.8			2.1
Silicates (as SiO$_2$)						48	110			130
Suspended Solids						0.29	<0.01			<0.01
Dissolved Solids						573	763			878

Figure 2-1. (Continued)

pond which is kept separate from the ponds receiving bottom ash slurries. The softened water is used for service water and for makeup water to the two cooling systems.

The water effluent from the overall operation comes from the overflow from the final polishing pond which is fed by the two boiler blowdown streams, the lime sludge disposal pond overflow, and the two bottom ash disposal pond overflows. The final polishing pond effluent is sent to the St. Charles River. The remaining system water losses are cooling tower evaporation and drift and other evaporative losses.

The first step in characterizing the chemistry of the Comanche water system is to examine the results of the spot samples taken. The measured species concentrations were input to the equilibrium program and several parameters were calculated which determine the tendency of the liquor sampled to form chemical scale and to absorb or desorb CO_2 from the atmosphere. Another parameter calculated checks the internal consistency of the sample and is a measure of the analytical accuracy.

One apparent inconsistency is that the softener feed has a silica concentration of 11 mg/ℓ whereas the cooling tower makeup (softener effluent) has a silica concentration of 56 mg/ℓ. The 11 mg/ℓ is consistent with Public Service of Colorado data but the 56 mg/ℓ in the cooling tower makeup is consistent with the 280 mg/ℓ in the cooling tower bottoms (about 5 cycles of concentration). This discrepancy was not resolved. The larger value of 56 mg/ℓ was used in this study for the makeup water to represent a worst case.

If silica problems are encountered at Comanche, hot or warm lime-soda softening should reduce silica. Another possibility is to use the magnesium bicarbonate process to remove silica. Silica removals of 48-84% were reported for this process in EPA report 600/2-76-285 entitled "Recovery of Lime and Magnesium in Potable Water Treatment" (TH-192).

Table 2-1 presents a summary of the parameters calculated for each of the samples taken at Comanche. Relative saturations for $CaCO_3$, $Mg(OH)_2$, and $CaSO_4 \cdot 2H_2O$ are given in the first three columns. These parameters indicate the tendency of the stream to form scale. Critical values for relative saturation of each species, above which scale formation is likely, are 2.5 for $CaCO_3$, 3.4 for $Mg(OH)_2$, and 1.3-1.4 for $CaSO_4 \cdot 2H_2O$ (see Appendix C).

TABLE 2-1. PARAMETERS CALCULATED BY EQUILIBRIUM PROGRAM FOR COMANCHE SAMPLES

Stream Name	Stream No.	Relative Saturations* $CaCO_3$	$Mg(OH)_2$	$CaSO_4 \cdot 2H_2O$	Equilibrium Partial Pressure of CO_2, atm x 10^4	% Residual Electroneutrality
Cooling Tower Makeup	14	0.0001	7.9×10^{-10}	0.028	12.2	+9
Cooling Tower Blowdown	15	0.0005	1.9×10^{-8}	0.31	5.6	-10
Ash Sluice Makeup	1	1.56	3.8×10^{-5}	0.031	2.2	-5
Ash Pond Inlet	23	0.41	1.1×10^{-6}	0.088	30.0	+8
Ash Pond Subsurface	--	0.66	7.0×10^{-6}	0.12	15.7	-2.4
Ash Pond Effluent	24	0.12	2.8×10^{-7}	0.11	31.4	-2
Polishing Pond Effluent	27	0.60	8.9×10^{-6}	0.17	10.7	-7

*Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$, about 2.5 for $CaCO_3$, and about 3.4 for $Mg(OH)_2$ (see Appendix C)

None of the streams sampled show a tendency to form $CaCO_3$, $Mg(OH)_2$, or $CaSO_4 \cdot 2H_2O$ scale. The highest $CaCO_3$ relative saturation was found in the ash sluice makeup water (1.56) but even that value was below the critical level. The relative saturations for the cooling tower blowdown indicate that the cycles of concentration may be increased somewhat since the gypsum relative saturation is only 0.31.

Equilibrium partial pressures of CO_2 above the liquor sampled were calculated by the equilibrium program and show the tendency of a stream to absorb or desorb CO_2 when in contact with the atmosphere. A value less than 3×10^{-4} atm, the equilibrium partial pressure of CO_2 in air, indicates a tendency to absorb CO_2 and a value greater indicates a tendency to desorb CO_2. The value for the cooling tower blowdown sample is very near 3×10^{-4} indicating that CO_2 equilibrium was essentially achieved in the cooling towers.

Percent residual electroneutrality is a parameter calculated to determine the internal consistency of each sample with pH specified. A value of ±15% is considered acceptable. All of the Comanche samples had a residual electroneutrality within ±10%. A more detailed description of how this parameter is calculated is presented in Appendix E.

2.2 Cooling System

The Comanche generating station has two cooling systems, one for each unit. The systems are identical and employ wet cooling towers for evaporative cooling. Water circulates at a design rate of 9240 ℓ/sec (146,400 GPM) between the condenser and cooling tower for each unit.

The circulating cooling water characteristics are controlled by the makeup water composition and by the amount of chemical additives introduced into the system. Sulfuric acid is added for pH control, and zinc polyphosphate is added to inhibit scaling.

The blowdown stream is maintained at a rate sufficient to keep dissolved species from concentrating to the point of saturation. Otherwise, scaling of the lines and equipment could result. The relationship between the blowdown rate, the cooling tower evaporation rate, the drift rate, and the amount of concentration that dissolved species undergo is expressed below:

$$C = \frac{E + B + D}{B + D}$$

C = cycles of concentration (number of times that dissolved species in the makeup water are concentrated in the circulating water)

E = evaporation rate

B = blowdown rate

D = drift rate (rate at which water is entrained in the vapor leaving the cooling tower)

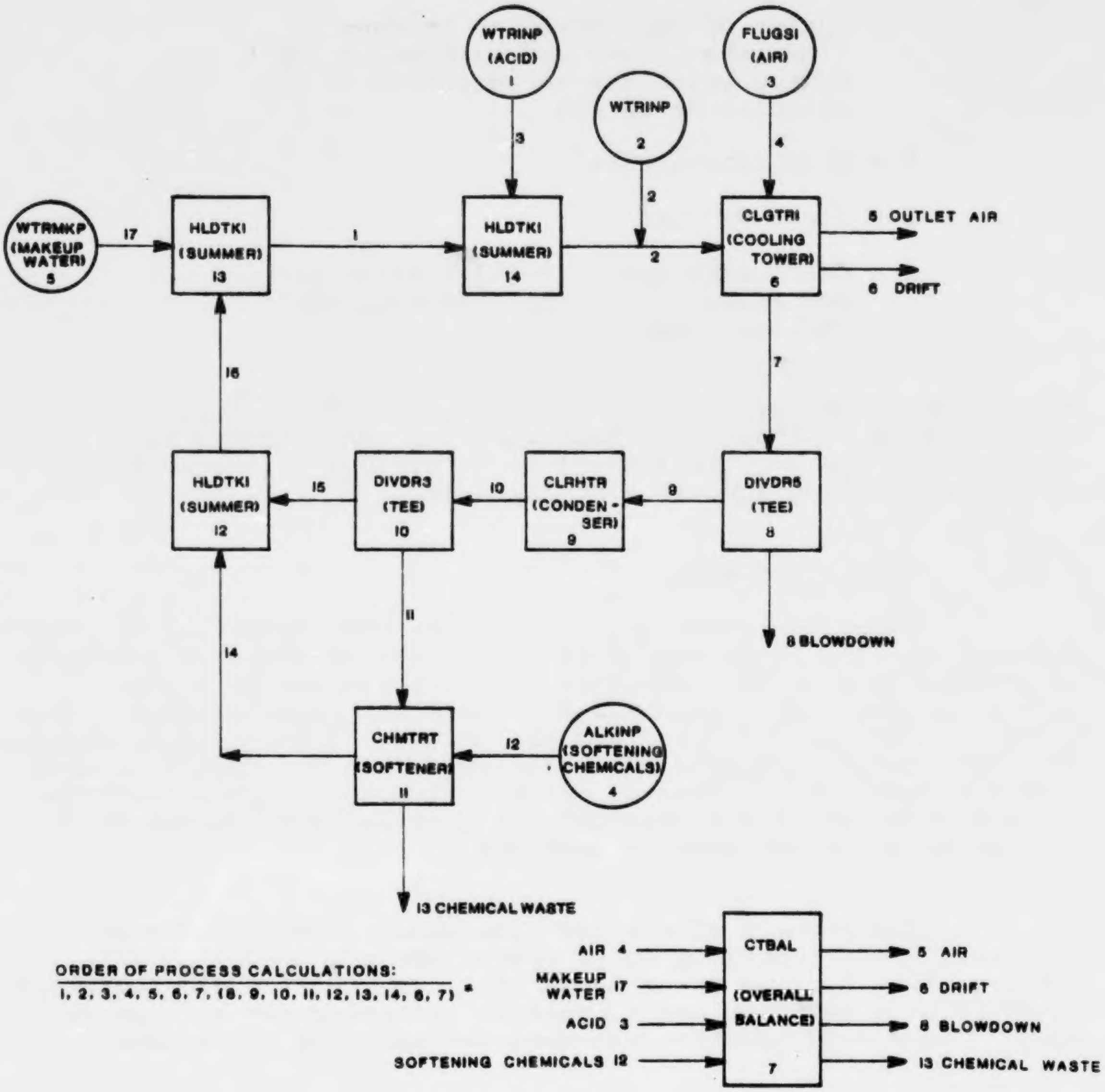
Present operation of the Comanche cooling system maintains the blowdown rate so that the makeup water is concentrated about 5 times (i.e., $C \cong 5$). This level is maintained to supply boiler refractory cooling and ash sluicing water.

2.2.1 Simulation Basis

Existing operations simulations were performed for the Comanche cooling tower system to verify the validity of the model in predicting scaling tendencies in the tower and/or condenser and to determine any potential for increased recycle/reuse. This section first briefly describes the computer model used to simulate the present Comanche water system. Then the inputs to this computer model (such items as process flowrates, concentrations, temperatures, etc.) are examined. A detailed description of the process model is included in Appendix E.

The process simulation flow scheme shown in Figure 2-2 was used to model cooling tower operations at Comanche. This is a generalized cooling tower model with capabilities of simulating sulfuric acid addition and slipstream softening for calcium removal. Only acid addition was used for existing operations.

Given the inputs of air flow, temperature and composition, makeup water composition, flow and temperature of the circulating water, drift rate, and cycles of concentration, the model performs iterative calculations around the cooling loop to determine the blowdown, evaporation and makeup rates, and compositions for all water streams. An acid addition rate is



ORDER OF PROCESS CALCULATIONS:

1, 2, 3, 4, 5, 6, 7, (8, 9, 10, 11, 12, 13, 14, 6, 7)^n

02-1527-1

Figure 2-2. Process simulation scheme for Comanche cooling tower system.

determined to keep the $CaCO_3$ relative saturation within a specified range. If slipstream softening is required (determined by model) the slipstream and chemical addition rates are calculated.

Several assumptions are inherent in performing this simulation with the subroutines shown in Figure 2-2. These assumptions are enumerated below:

1) Equilibrium exists between CO_2 and H_2O in the atmosphere and cooling tower exit water.
2) The temperature of the cooled water stream approaches the wet bulb temperature of ambient air within a predictable range.
3) The compositions and temperatures of the cooled water and drift streams are equal.
4) Ionic reactions taking place in the liquid phase are rapid and thus at equilibrium.

The assumption involving the temperature of the cooled water stream is a recognized design parameter in cooling tower evaluation and gives a good approximation. The assumption concerning the temperature and composition of the drift stream should be very close to actuality, as is the assumption in regard to H_2O gas-liquid equilibrium. The assumption with regard to CO_2 equilibrium is conservative since the partial pressure of CO_2 in actual cooling towers tends to be greater than the equilibrium value. The lower equilibrium concentration of carbonate species assumed in the model causes the pH to be slightly higher in the model than in actual operation. The higher pH causes the relative saturation of $CaCO_3$ to increase more than the lowered carbonate species concentration causes it to decrease.

The data used as input to this model is presented in Table 2-2. Some of this information was obtained directly from PSC while other inputs were calculated from PSC data, local meteorological data, and sample analyses. The air flows were obtained from PSC and adjusted to a representative temperature and composition by means of local climatological data. The ambient

TABLE 2-2. INPUT DATA FOR COMANCHE COOLING TOWER SIMULATIONS

	Winter	Summer
FLOWS		
Air, m^3/hr	2.7×10^7	2.7×10^7
(ACFM)	(1.6×10^7)	(1.6×10^7)
Drift, ℓ/sec	9.0	9.0
(GPM)	(142)	(142)
Circulating Water, ℓ/sec	9,240	9,240
(GPM)	(146,400)	(146,400)
TEMPERATURES		
Ambient Air, °C	0	22.2
(°F)	(32)	(72)
Approach, °C	11.1	8.3
(°F)	(20)	(15)
Condenser ΔT, °C	14.1	14.4
(°F)	(26)	(26)
Wet Bulb, °C	-2.8	17.8
(°F)	(27)	(64)
Condenser Outlet, °C	22.8	40.6
(°F)	(73)	(105)
ADDITIONAL DATA		
Relative Humidity, %	53	68
Cycles of Concentration	5	5
Makeup Water Composition, mg/ℓ		
Calcium	36.5	36.5
Magnesium	10.2	10.2
Sodium	26.2	26.2
Chloride	5.3	5.3
Carbonate (as $CO_3^=$)	5.4	5.4
Sulfate (as $SO_4^=$)	163	163
Nitrate (as NO_3)	12.4	12.4

air wet bulb temperatures were derived from climatological data from the National Oceanic and Atmospheric Administration averages (NA-166). The water makeup composition was obtained from the spot sample and adjusted to minimize residual electroneutrality (see Appendix E).

2.2.2 Simulation Results

This section gives the results of simulating the existing operations at Comanche. The simulations are based on the heavy-load summer conditions and heavy-load winter conditions, whose operating parameters have been described in the previous sections. The simulation results are compared with the results coming from the chemical analyses in order to evaluate the performance of the computer process model in giving a reasonable approximation of typical Comanche operating conditions.

Table 2-3 is a summary of the most important simulation results for the existing operations of the Comanche cooling system along with the plant data for actual operation.

The blowdown flow for summer operation is within the data range reported by PSC. The winter blowdown is slightly lower probably due to differences in climatological data. The blowdown stream pH values compare well (6.3 *versus* 6.4). When the sample blowdown composition is compared with simulation compositions for summer and winter operations, however, it appears that the measured concentrations are for the most part greater than the simulation concentrations. The difference between measured and simulation concentrations for calcium, magnesium, chloride, sulfate, and carbonate indicates that the Comanche cooling system was operating at a concentration factor in excess of the value of 5.0 used in the simulations. Using the measured concentrations, an actual concentration factor of about 5.8 is indicated. This difference is well within the range of typical operation, especially since the measurements may not have been taken at the heavy-load conditions assumed for the simulations.

The major discrepancy in the blowdown composition results involves the nitrate ion, whose measured concentration does not agree very well with its simulation concentrations. However, the measured value of the makeup concentration (12.4 mg/ℓ) is not consistent with the measured blowdown composition (16 mg/ℓ) either, if a concentration factor of 5.0 or above is assumed. Therefore, analytical uncertainties or errors are indicated in the case of the nitrate species. The problem with the nitrate

TABLE 2-3. COMANCHE EXISTING COOLING TOWER OPERATIONS

Cooling Tower Blowdown	Plant Data	Simulations (5 cycles of concentrations) Case 1 Winter Operation	 Case 2 Summer Operation
Flow, ℓ/sec per tower	31.5 - 41.3	24.6	37.8
(GPM)	(500 - 655)	(390)	(600)
pH	6.3	6.42	6.45
Composition, mg/ℓ			
Calcium	205	181	181
Magnesium	65.5	50.9	50.8
Sodium	89	131	131
Chloride	53	26.5	26.5
Sulfate (as $SO_4^{=}$)	965	824	824
Carbonate (as $CO_3^{=}$)	2.7	2.2	1.85
Nitrate (as NO_3^{-})	16	61.8	61.8
Relative Saturations*			
$CaCO_3$	5.0×10^{-4}	2.3×10^{-4}	8.2×10^{-4}
$CaSO_4 \cdot 2H_2O$	0.31	0.30	0.25
Partial Pressure CO_2, atm	5.6×10^{-4}	3.3×10^{-4}	3.6×10^{-4}

*Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C) concentration serves to explain the lesser discrepancies with the chloride and sodium ions, because these ions were adjusted in the makeup composition used as a simulation input. Any errors in the nitrate concentration, therefore, influence the simulation blowdown values of sodium and chloride.

Although the simulation results of the sodium, chloride, and nitrate ions do not compare precisely with their measured values, the discrepancies do not severely limit the usefulness of the process model in simulating the cooling system operation. These ions do not form ionic pair bonds comparable in strength to the $CaSO_4$ and $CaCO_3$ bonds. Therefore, any perturbations in the ions respective concentrations (assuming that the pH is kept constant) should not greatly influence the Ca^{++}, SO_4, and $CO_3^=$ activities and resultant scaling potentials. This is borne out when the relative saturations of $CaSO_4 \cdot 2H_2O$ and $CaCO_3$ are examined.

The relative saturation of $CaCO_3$ with the measured blowdown composition (5×10^{-4}) is in good agreement with the summer and winter simulation values (8.2×10^{-4} and 2.3×10^{-4}). The relative saturation of $CaSO_4 \cdot 2H_2O$ also agrees well. The measured composition's relative saturation for $CaSO_4 \cdot 2H_2O$ is 0.31, the simulation values are 0.25 for the summer case and 0.30 for the winter case. The comparison becomes even closer if, as mentioned above, the measured composition corresponds to a concentration factor slightly greater than that used for the simulation cases.

Judging from the agreement between the measured composition and the simulation results, the computer process model can be used to adequately simulate typical cooling system behavior. The simulation results indicate a potential for reducing cooling water requirements by increasing the cycles of concentration. The effects of increasing the cycles of concentration with respect to cooling tower operation and the subsequent use of blowdown water for ash sluicing are the subject of the following section. The sensitivity of the cooling system to increases of $SO_4^=$ in the makeup water is also investigated to determine the operational effects of poorer quality makeup water.

2.3 Ash Disposal System

The ash disposal system at the Comanche generating station consists of two ash ponds with a surface area of about 5060 m^2 (54,000 ft^2) each. Only bottom ash is being sluiced into the ponds at present. The fly ash is trucked away in a dry form.

The bottom ash is sluiced to the ash ponds at about 1 wt. % solids. The sluicing is intermittent; bottom ash is pulled from the ash hopper about six hours per day. The sluice water comes from two sources: blowdown from the cooling system and untreated water from the plant raw water reservoir. The flow rates for these streams were averaged over a 24-hour period to give representative flow rates for simulating a continuous system.

Part of the cooling system blowdown stream is diverted for use as boiler refractory cooling water. This water subsequently flows down into the bottom ash hoppers where an overflow stream is sent to the ash ponds. But when bottom ash is being pulled, the refractory cooling water goes out in the bottom ash sluice stream.

The bottom ash sluice stream travels to the ash pond at about 210 cm/sec (7 ft/sec). The sluice lines for the two boiler units are 760 m and 590 m (2,500 and 1,930 ft) long, giving line retention times of about 5.9 and 4.6 minutes, respectively.

No simulations of the existing ash handling systems were performed but in the next section the alternatives looked at do include wet sluicing of the ash and the appropriate simulations were used to study the alternatives.

3.0 TECHNICAL ALTERNATIVES

Water recycle/reuse alternatives for the Comanche plant are presented in this section. The Comanche water system was divided into two subsystems for purposes of simulation. One subsystem consists of the cooling towers, with associated treatment facilities and condensers. The other subsystem consists of the ash disposal operations.

The operating characteristics of the cooling system are examined first. Then the ash handling system is analyzed in the context of the possible range of cooling system blowdown streams available for sluicing. Water recycle/reuse alternatives, therefore, will be based on an overall picture of the Comanche water system.

3.1 Cooling Towers

Before a water management strategy can be made for the Comanche ash sluicing system, the cooling system must be fully characterized with respect to the effects of increasing cycles of concentration. This is necessary to provide information about the cooling tower blowdown, which is used as sluice water. Also. information is needed regarding the cooling system sensitivity, i.e., how changes in makeup water composition affect the system. The scaling potential of $CaSO_4 \cdot 2H_2O$ and $CaCO_3$ are the most crucial areas concerning the operation of the towers at higher cycles of concentration.

In order to characterize the cooling system, simulations were run which varied the cycles of concentration of the recirculating cooling water by adjusting the blowdown flow rate. Additional simulations were subsequently run in which the concentration of $SO_4^=$ in the makeup water was doubled. The differences in system behavior between the first set of simulations using the makeup water compositions determined by sample analysis and the second set of simulations using the makeup water with increased sulfate serve as a measure of the sensitivity of the Comanche cooling system to changes in river water quality with respect to sulfate.

Section 3.1.1 is concerned with the simulation basis used with the process model in making the computer characterization of the Comanche cooling towers. Section 3.1.2 and 3.1.3 are discussions of the results of these simulations.

Section 3.1.2 addresses the changes in the cooling system arising from increasing the cycles of concentration. The changes of particular interest are the changes in the approach toward scaling of the chemical species in the recirculating cooling water and the change in the acid rate required to maintain pH control.

Section 3.1.3 discusses the changes which result from using makeup water with twice the sulfate concentration used in the previous simulations. Simulations were run at different cycles of concentration as before in order to determine how the sulfate concentration increase affects the approach to scaling.

3.1.1 Simulation Basis

The basis for the simulations to characterize the Comanche cooling towers is the same as discussed earlier in Section 2.2.1. The process model is unchanged. The sole differences between the existing operations simulation discussed earlier and these alternative operations simulations lie in altering the computer inputs to the process model.

The first series of calculations were directed at determining the effects of increasing the cycles of concentration. The second series of simulations were conducted in a similar manner, except that the $SO_4^{=}$ concentration was doubled in the water makeup stream. The Na^+ ion was also increased in order to maintain a constant pH. (The net effect was to increase sulfate concentration by addition of Na_2SO_4 to the makeup water.

All of the alternative cooling tower simulations were performed for summer operation of the cooling towers because summer conditions represent the case of maximum blowdown rates. Increased evaporation needed during the summer months requires an increase in blowdown rate to maintain a constant concentration factor. Therefore, summer operation represents a conservative or limiting case. For a given makeup water composition and blowdown rate, the summer operation results in a higher concentration factor than does the winter operation.

3.1.2 Effect of Increased Cycles of Concentration

Simulation results of cooling tower operations at 5.0, 7.6, and 15.0 cycles of concentration are presented in

Table 3-1. Sulfuric acid treatment was used to maintain a slightly acidic blowdown pH, which represents typical Comanche practice. Additional acid treatment was not needed to control $CaCO_3$ scale, because $CaCO_3$ relative saturation remained well below the critical scaling value of 2.5 (Appendix C) for all three cases.

Although $CaCO_3$ scaling is not a problem for operation at 15.0 cycles of concentration, $CaSO_4 \cdot 2H_2O$ does approach the critical scaling value range for relative saturation of 1.3-1.4 at this level of concentration. The relative saturation of $CaSO_4 \cdot 2H_2O$ *versus* cycles of concentration is plotted in Figure 3-1. As might be expected for such a relatively dilute aqueous system, the relative saturation behaves quite linearly with respect to increasing the cycles of concentration.

Operating the cooling towers at higher cycles of concentration may cause species other than gypsum or calcium carbonate to become supersaturated and possibly form scale. Table 3-2 presents the calculated relative saturations at 5.0, 7.6, and 15 cycles of concentration for the important phosphate and silica species.

None of the phosphate species were supersaturated at 15 cycles of concentration, the highest value being about 0.5 for $CaHPO_4$. All of the silica solids are subsaturated for all cases except for SiO_2 and $Mg(SiO_2)_3(OH)_2$. Existing operations (5 cycles) shows a relative saturation of 1.36 for SiO_2 but no evidence of scaling exists. This suggests that a critical value greater than one exists for SiO_2 as well as $CaCO_3$, $Mg(OH)_2$, and $CaSO_4 \cdot 2H_2O$. The magnitude of this value is unknown, so that increasing the cycles of concentration in the towers at Comanche could cause scaling problems.

The relative saturation of $Mg(SiO_2)_3(OH)_2$ (sepiolite) is 0.54 for existing operations but rises to about 1.8 for 7.6 cycles and 31. for 15 cycles. The critical value for this species also is not known, so that the scaling limit for cycles of concentration is also unknown.

In light of the above discussion, additional testing should be performed to more accurately determine the control limits for magnesium-silica solids before implementing water recycle/reuse alternatives requiring increased cycles of concentration in the cooling towers. Any significant increase in

TABLE 3-1. EFFECTS OF INCREASED CYCLES IN COMANCHE COOLING TOWERS*

	Existing Operations	Increased Cycles of Concentration	
Cycles of Concentration	5.0	7.6	15.0
Makeup Water Rate, ℓ/sec	235	216	200
(GPM)	(3720)	(3430)	(3190)
Acid Addition Rate, kg/day**	48.1	41.3	40.5
(lb/day)	(106)	(91.0)	(89.3)
Blowdown			
Flow, ℓ/sec	38	20	4.5
(GPM)	(600)	(310)	(70)
pH	6.5	6.9	7.0
Composition, mg/ℓ			
Calcium	181	275	540
Magnesium	50.8	77.1	151
Sodium	131	198	388
Chloride	26.5	40.2	78.8
Carbonate (as $CO_3^=$)	1.9	3.8	4.6
Sulfate (as $SO_4^=$)	824	1250	2450
Nitrate (as NO_3^-)	61.8	93.6	184
Temperature, °C	26.1	26.1	26.1
(°F)	(79)	(79)	(79)
Relative Saturations***			
$CaCO_3$	8.8×10^{-4}	8.2×10^{-4}	0.018
$CaSO_4 \cdot 2H_2O$	0.25	0.43	0.98

* All flows are for one unit.

** As 100% H_2SO_4

*** Critical values, above which scaling potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C)

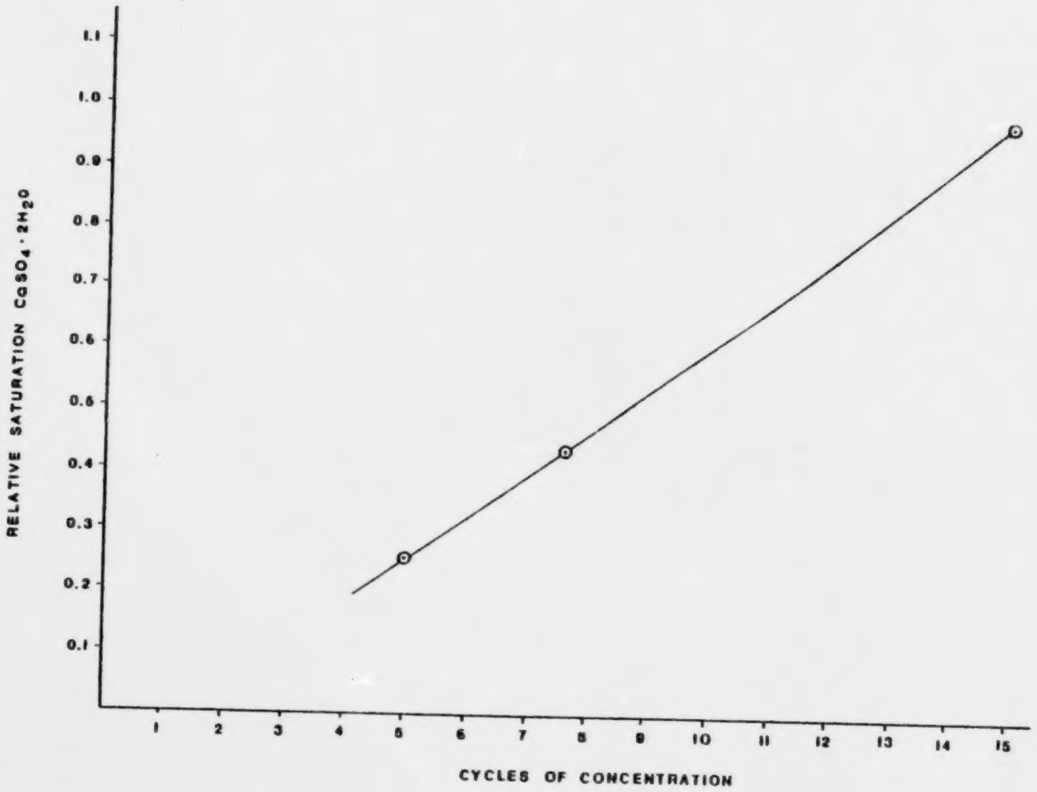


Figure 3-1. Gypsum relative saturation as a function of cycles of concentration at Comanche.

TABLE 3-2. RELATIVE SATURATIONS OF PHOSPHATE AND SILICA SOLIDS IN COMANCHE COOLING TOWERS

Cycles of Concentration	5	7.6	15.0
Relative Saturations			
$CaHPO_4$	.117	.192	.486
$Ca_3(PO_4)_2$	.0011	.0027	.038
SiO_2	1.36	2.06	4.07
$Mg_2Si_3O_5(OH)_6$	6.6×10^{-5}	2.0×10^{-4}	7.7×10^{-3}
$Mg_3Si_2O_5(OH)_4$	6.3×10^{-5}	1.1×10^{-4}	5.1×10^{-3}
$Mg(SiO_2)_3(OH)_2$	0.54	1.79	31.0
CaH_2SiO_4	7.87×10^{-6}	1.09×10^{-5}	4.76×10^{-5}
$Ca(H_3SiO_4)_2$	5.0×10^{-4}	1.05×10^{-3}	9.12×10^{-3}

the cooling system cycles of concentration may necessitate additional chemical treatment of the makeup water or a slipstream from the circulating water to reduce the silica concentration. The makeup water concentration may be reduced by using hot lime-soda ash treatment (RO-266) or the magnesium bicarbonate process (TH-192) instead of the present lime treatment.

3.1.3 Effect of Sulfate Concentration in the Makeup Water

Three simulation runs were made at 5.0, 7.6, and 13.0 cycles of concentration for makeup water containing twice as much sulfate as used for the existing operations simulations. The results of these runs are presented in Table 3-3. As in the simulations presented in the previous section, acid addition rates were calculated to produce a slightly acidic blowdown stream.

As can be seen from the relative saturations given in Table 3-3, the $CaCO_3$ relative saturation is far removed from its critical scaling value due to the fact that almost all of the Ca^{++} ions are associated with $SO_4^=$ ions. The $CaSO_4 \cdot 2H_2O$ relative saturations for the simulations using the makeup water with the doubled sulfate concentration are larger than the previous simulations using the sample makeup water but are not larger by a factor of two. Apparently, the $SO_4^=$ activity is not doubled by increasing the sulfate concentrations by a factor of two. With the makeup water containing twice as much sulfate, a relative saturation of 1.0 is reached at about 13 cycles of concentration, whereas this high a value for $CaSO_4 \cdot 2H_2O$ relative saturation was not reached until 15 cycles of concentration with the existing makeup water quality.

In both sets of simulations the acid addition rate was found to be insensitive to the number of cycles of concentration. In every case an acid rate of about 43 kg/day (95 lb/day) was sufficient to maintain a neutral or slightly acidic blowdown stream.

3.2 Ash Handling Systems

Three alternatives for ash handling at Comanche were studied: (1) once-through sluicing of bottom ash and fly ash, (2) the recirculation of ash pond liquor, and (3) bottom ash sluicing and dry fly ash disposal. Fly ash sluicing is included as well as the existing bottom ash sluicing for the first two alternatives. For fly ash sluicing, the effects of CO_2 transfer in the pond and in the sluice tank are examined as well as the scaling potentials of the system.

TABLE 3-3. EFFECTS OF MAKEUP WATER SULFATE CONCENTRATION* ON COMANCHE COOLING TOWER OPERATION

Cycles of Concentration	5.0	7.6	13.0
Makeup Water Rate, ℓ/sec	235	216	203
(GPM)	(3720)	(3430)	(3220)
Acid Addition Rate, kg/day**	43.0	43.7	43.0
(lb/day)	(94.8)	(96.4)	(94.8)
Blowdown			
Flow, ℓ/sec	38	20	6.7
(GPM)	(600)	(310)	(105)
pH	7.0	6.9	6.7
Composition, mg/ℓ			
Calcium	181	275	469
Magnesium	50.8	77.1	131
Sodium	520	789	1340
Chloride	26.5	40.2	68.5
Carbonate (as $CO_3^=$)	1.9	3.8	4.7
Sulfate (as $SO_4^=$)	1640	2480	4220
Nitrate (as NO_3^-)	61.8	93.6	159
Temperature, °C	26.1	26.1	26.1
(°F)	(79)	(79)	(79)
Relative Saturations			
$CaCO_3$	0.0055	0.0056	0.0058
$CaSO_4 \cdot 2H_2O$	0.33	0.55	1.01

---

[*] Sulfate concentration of 326 mg/ℓ as opposed to sampled level of 163 mg/ℓ

[**] As 100% H_2SO_4

[***] Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C)

This section first discusses the simulation basis for these simulations, including a brief description of the process model and the input data. The simulation results are then presented and discussed.

3.2.1 Simulation Basis

The basis for simulation of alternative ash sluicing operations at Comanche is presented in this section. A description of the process model utilized and the important assumptions made is first given. Then the input data used in these simulations is summarized.

The process model used to simulate both once-through and recirculating ash sluice systems at Comanche is shown in Figure 3-2. The model uses information about the compositions and flows of the makeup water and fly and bottom ash as well as the percent solids in the sludge and pond evaporation as inputs. From this information the flows and compositions of all the streams in Figure 3-2 are calculated. A detailed description of the ash sluicing model is given in Appendix E.

Several assumptions are inherent in performing ash sluicing simulations with the subroutines outlined above. These assumptions are listed below:

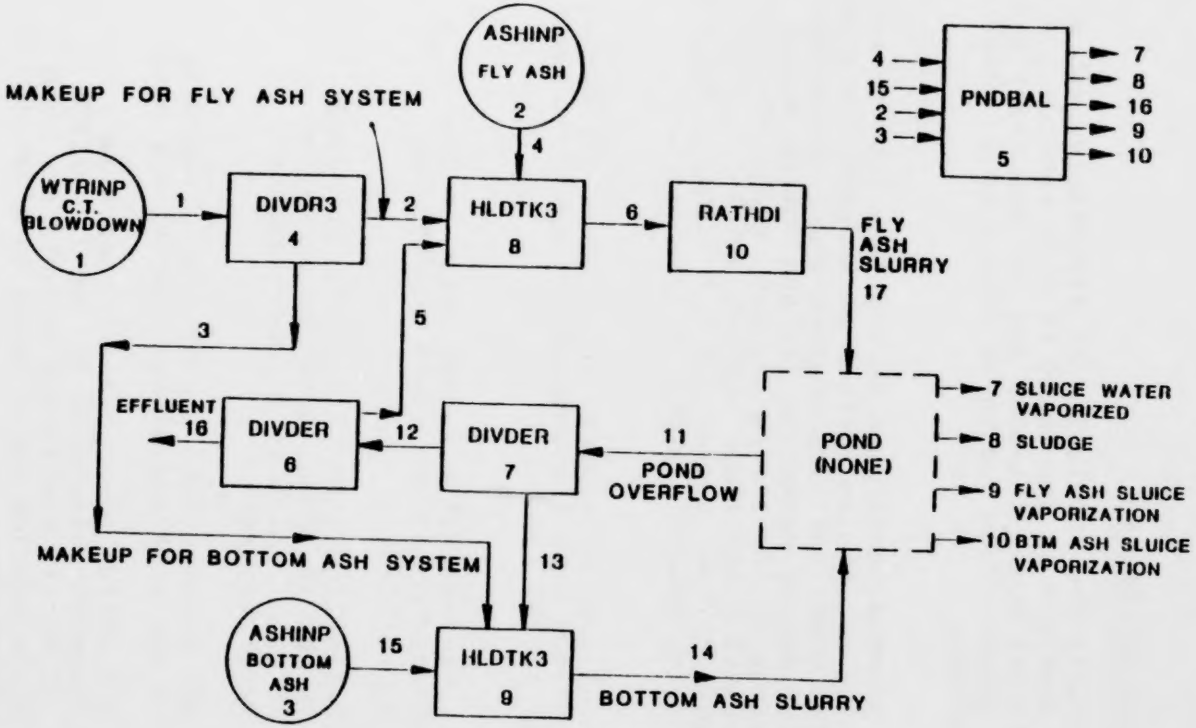
1) Ionic reactions taking place in the liquid phase are rapid and thus at equilibrium.

2) Solid-liquid equilibrium is achieved in the ash pond, with the exception of $CaSO_4$ which is allowed to remain supersaturated.

3) Ash dissolution is essentially complete by the time the slurry reaches the pond.

4) All solids precipitation occurs in reaction vessels or the pond. RATHD1 calculates nucleation amounts and then precipitation rates based on kinetic expressions.

5) Subroutine RATHD1 models nucleation as an instantaneous rate if the species'



ORDER OF PROCESS CALCULATION: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 *

Figure 3-2. Process simulation scheme for Comanche ash sluicing system.

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relative saturation exceeds the critical value. Nucleation is allowed such that the various species' relative saturations are returned to their respective critical levels. At this point, no further nucleation is allowed.

The input data used in simulating a once-through ash sluicing system and a recirculating ash sluicing system at the Comanche plant are given in Tables 3-4 and 3-5. The fly ash flow rate and the bottom ash flow rate were taken to be 78% and 22%, respectively, of the total ash flow rate, which was calculated from Public Service of Colorado information.

Sluice water rates shown in Table 3-4 were calculated based on (1) the use of the existing blowdown rate, taken at 5.0 cycles of concentration, and (2) a slurry solids content of about 10% for the fly ash stream. The sluice water composition corresponds to the existing operations blowdown composition.

The soluble species data for the fly ash were obtained from ash characterization studies performed in support of this program (Appendix L). The results of the leaching studies performed in this program were used. Calculations performed to obtain the soluble species amounts are presented in Appendix L.

The sluice makeup and sluice recycle water flows given in Table 3-5 are based on sluicing the fly ash at about 10 wt. % solids using 90% cooling tower blowdown and 10% ash pond recycle water. Bottom ash is sluiced at about 4 wt. % solids using only pond recycle water. The boiler refractory cooling water flow rate is unchanged from its design value of 16.4 ℓ/sec (260 GPM). The fly ash soluble species amounts were assumed to remain constant.

3.2.2 Once-Through Ash Sluicing System

The simulation results for once-through fly ash sluicing at Comanche using cooling system blowdown as sluice water are given in Table 3-6. The simulation is based on blowdown water corresponding to cooling tower operation at 5.0 cycles of concentration. No transfer of CO_2 was permitted between the atmosphere and the sluice liquor at any point within the sluicing system. The effects of CO_2 transfer will be discussed in Section 3.2.4.

TABLE 3-4. COMANCHE ONCE-THROUGH ASH SLUICING INPUT DATA

Flow Rates (per unit)		
Fly Ash, kg/min (lb/min)	151.	(333.7)
Bottom Ash, kg/min (lb/min)	45.	(99.)
Fly Ash Sluice Water, ℓ/sec (GPM)	21.7	(344)
Bottom Ash Sluice Water, ℓ/sec (GPM)	16.4	(260)
Pond Evaporation, ℓ/sec (GPM)	.15	(2.4)
Sluice Water Composition	mg/ℓ	
(Cooling Tower Blowdown @ 5 Cycles)		
Calcium	181.7	
Magnesium	50.86	
Sodium	130.5	
Chloride	26.5	
Carbonates, as $CO_3^=$	1.85	
Nitrate, as NO_3^-	61.8	
Sulfate, as $SO_4^=$	824.5	
Pond Deposits (40 wt. % solids)		
Soluble Ash Species	(Fly Ash) wt. %	
CaO	2.287	
MgO	0.287	
Na_2O	0.041	
$CaSO_4$	1.010	

TABLE 3-5. COMANCHE RECIRCULATING ASH SLUICE INPUT DATA (10% Recycle in Fly Ash System)

Flow Rates (per unit)		
Fly Ash, kg/min (lb/min)	151	(333.7)
Bottom Ash, kg/min (lb/min)	45	(99)
Fly Ash Sluice Makeup, ℓ/sec (GPM)	19.6	(310)
Bottom Ash Sluice Makeup, ℓ/sec (GPM)	0.0	(0)
Fly Ash Sluice Recycle, ℓ/sec (GPM)	2.2	(34)
Bottom Ash Sluice Recycle, ℓ/sec (GPM)	19.6	(310)
Pond Evaporation, ℓ/sec (GPM)	.15	(2.4)
Sluice Water Composition (Cooling Tower Blowdown @ 7.6 Cycles)	mg/ℓ	
Calcium	275	
Magnesium	77.1	
Sodium	198	
Chloride	40.2	
Carbonates, as $CO_3^=$	3.8	
Nitrate, as NO_3^-	93.6	
Sulfate, as $SO_4^=$	1250.	
Pond Deposits (40 wt. % solids)		
Soluble Ash Species	(Fly Ash) wt. %	
CaO	2.287	
Na_2O	0.041	
MgO	0.077	
$CaSO_4$	1.010	

TABLE 3-6. COMANCHE ONCE-THROUGH ASH SLUICING SIMULATION RESULTS*

	Fly Ash Slurry	Ash Pond Overflow
Flow, ℓ/sec	21.5	32.7
(GPM)	(356)	(518)
Composition, mg/ℓ		
Calcium	2,450.	1290.
Magnesium	106.	0.01
Sodium	167.	153.
Chloride	27.	27.
Sulfate, as $SO_4^=$	1,670.	1300.
Carbonate, as $CO_3^=$	1.9	0.7
Nitrate, as NO_3^-	62.	62.
Temperature, °C	40.6	17.8
(°F)	(105)	(64)
Relative Saturations **		
$CaCO_3$	5.37	1.0
$CaSO_4 \cdot 2H_2O$	1.24	1.1
$Mg(OH)_2$	35,360.	1.0
pH	12.3	12.7

* No CO_2 transfer in the system.

** Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$, about 2.5 for $CaCO_3$, and about 3.4 for $Mg(OH)_2$ (see Appendix C)

The relative saturation of $CaSO_4 \cdot 2H_2O$ in the fly ash slurry indicates that gypsum scaling will not occur in the once-through ash sluice system. The calculated relative saturation of 1.24 is below the critical scaling level of 1.3-1.4. But a strong probability of scaling exists for calcium carbonate and magnesium hydroxide in the fly ash slurry. The calculated values for relative saturation of $CaCO_3$ and $Mg(OH)_2$ are larger than their respective critical values of 2.5 and 3.4 (see Appendix C).

A reaction tank installed before the sluice line can possibly be used to minimize the scaling of $CaCO_3$ and $Mg(OH)_2$ in the sluice line. This will permit a significant portion of the solids to be formed within the reaction tank as opposed to the line.

In order to facilitate fly ash sluice water mixing and precipitation of solids in the fly ash slurry tanks two small tanks can be used instead of a single large tank. This will minimize channeling in the slurry tank. Although the slurry tank may be designed to guard against fouling in the slurry line, some scaling of $CaCO_3$ and $Mg(OH)_2$ can be expected. A possible measure to prevent fouling would be to periodically flush the line with a relatively low pH water stream. Water with a pH of 6 to 7 should be adequate to remove solid $CaCO_3$ and $Mg(OH)_2$ because these compounds readily dissociate in this pH range. One possible source of this flush water is cooling system blowdown, which is typically neutral or slightly acidic.

3.2.3 Recirculating Ash Sluicing System

The configuration examined to determine the effects of recirculating ash pond water as sluice water uses the blowdown from the cooling system to sluice fly ash with only 10% of the sluice water recycled and uses ash pond water to sluice bottom ash.

As in the once-through simulation discussed in the previous section, no CO_2 transfer between the atmosphere and the process liquor was permitted at any point in the system. The effects of CO_2 transfer are discussed in Section 3.2.4.

The results of the simulation are presented in Table 3-7. As shown, strong potential for gypsum scaling exists throughout the system. The fly ash slurry gypsum relative

TABLE 3-7. COMANCHE RECIRCULATING ASH SLUICING SIMULATION RESULTS*

	Fly Ash Sluice Water Recycle	Fly Ash Slurry	Ash Pond Overflow
Flow, ℓ/sec	2.1	21.5	14.4
(GPM)	(34)	(342)	(229)
Composition, mg/ℓ			
Calcium	1580.	2680.0	1580.0
Magnesium	0.01	124.0	0.01
Sodium	240.	240.0	240.0
Chloride	40.8	40.4	40.8
Sulfate, as $SO_4^=$	2190.	2180.0	2190.0
Carbonate, as $CO_3^=$	.73	3.5	.73
Nitrate, as NO_3^-	94.	94.0	94.0
Relative Saturations**			
$CaCO_3$	1.0	6.46	1.0
$CaSO_4 \cdot 2H_2O$	1.83	1.76	1.83
$Mg(OH)_2$	1.0	42,750.0	1.0
pH	12.7	12.7	12.7

*Makeup water to sluice system is cooling tower blowdown at 7.6 cycles of concentration.

**Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$, about 2.5 for $CaCO_3$, and about 3.4 for $Mg(OH)_2$ (see Appendix C) saturation of 1.76 exceeds the critical range for scale formation of 1.3-1.4. A potential solution to the problem of $CaSO_4 \cdot 2H_2O$ scaling with this configuration is to treat a portion of the cooling tower blowdown prior to the ash sluicing system. Two types of treatment were examined: (1) lime softening of the entire cooling tower blowdown for calcium removal and (2) brine concentration of 50% of the tower blowdown. A comparison of the effects of these treatment options is shown in Table 3-8.

Lime treatment of the fly ash sluice makeup water is not sufficient to prevent gypsum scaling in the sluice line. The $CaSO_4 \cdot 2H_2O$ relative saturation for this case is 1.74, which greatly exceeds the critical range for scale formation of 1.3-1.4. However, brine concentration of 50% of the makeup water results in a gypsum relative saturation of 1.29 in the fly ash slurry which is just below the critical range for scale formation. This lower scaling potential is due to the removal of sulfate as well as calcium from the makeup water, whereas with lime treatment, only calcium removal is realized.

Another possibility which may lower gypsum scale potential in the slurry is gypsum desupersaturation in the pond. The degree of desupersaturation that may occur in the pond cannot be accurately quantified but will depend on the degree of turbulence in the pond and on the residence time in the pond. The greater the degree of mixing in the pond due to thermal gradients or wind turbulence, the more desupersaturated the liquor will become. Longer residence times will also encourage gypsum precipitation.

However, the lack of suspended $CaSO_4 \cdot 2H_2O$ crystals in the pond will discourage any precipitation and therefore, limit the degree of desupersaturation. An additional case allowing $CaSO_4 \cdot 2H_2O$ precipitation to equilibrium (relative saturation of 1.0) was run but since only 10% of the fly ash sluice water is recycled, the gypsum relative saturation in the slurry was only reduced to 1.68 from 1.76. Thus, the level of supersaturation in the pond will have only a very small effect on the slurry gypsum relative saturation with this configuration.

Since calcium and sulfate in the makeup water are the limiting constituents, an alternative treatment is to remove calcium and sulfate by controlled gypsum precipitation. Operation of this treatment is very similar to the situation encountered in lime/limestone SO_2 scrubbing where gypsum is precipitated in

TABLE 3-8. COMANCHE FLY ASH SLUICE MAKEUP WATER TREATMENT EFFECTS

	Fly Ash Slurry	
	Treatment A*	Treatment B**
Composition, mg/ℓ		
Calcium	2,550.0	2,660.0
Magnesium	137.0	99.0
Sodium	239.0	140.0
Chloride	40.0	20.0
Sulfate, as $SO_4^=$	2,180.0	1,560.0
Carbonate, as $CO_3^=$	3.8	1.9
Nitrate, as NO_3^-	94.0	47.0
Relative Saturations* **		
$CaCO_3$	6.97	3.61
$CaSO_4 \cdot 2H_2O$	1.74	1.29
$Mg(OH)_2$	45,070.0	37,500.0
pH	12.7	12.8

* Makeup water treated with lime for Ca removal.

** 50% of makeup water treated with brine concentration.

*** Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$, about 2.5 for $CaCO_3$, and about 3.4 for $Mg(OH)_2$ (see Appendix C) a reaction tank with $CaSO_4 \cdot 2H_2O$ solids recirculated. Calcium and sulfate may be removed in this treatment alternative in two steps: (1) addition of lime to precipitate gypsum in a tank with recirculating $CaSO_4 \cdot 2H_2O$ seed crystals and (2) addition of CO_2 to precipitate $CaCO_3$. However, this is not proven technology for water treatment and pilot studies would have to be conducted to size process vessels before a full-sized installation could be considered.

Although treatment of the makeup water will prevent gypsum scale, the relative saturations of $CaCO_3$ and $Mg(OH)_2$ are still above the respective critical levels of 2.5 and 3.4. As in the once-through sluicing scheme, $CaCO_3$ and $Mg(OH)_2$ scale formation in the slurry line may be reduced by installing a reaction tank prior to the sluice line. The sizing of the reaction tanks will be critical to the successful operation of this ash sluicing configuration. Additional data taken on a pilot scale should be gathered before implementing this technical alternative. Also, flush water may possibly be used to clean $CaCO_3$ and $Mg(OH)_2$ deposits at periodic intervals as suggested for once-through sluicing. Pilot studies to determine the level of acid washing necessary to prevent plugging should be conducted before this alternative is implemented.

The recirculating ash sluice system with makeup water treatment will produce an ash pond overflow of about 14.4 ℓ/sec (229 GPM) per unit which is reduced from the 32.7 ℓ/sec (518 GPM) flow per unit for the once-through alternative. Treatment of the ash pond overflow to achieve zero discharge can be accomplished by a brine concentrator or a brine concentrator/reverse osmosis system. The clean water produced by such treatment could be recycled as boiler makeup water and cooling tower makeup water.

3.2.4 Effect of Carbon Dioxide Mass Transfer

Five additional cases were studied to determine the effects on the operation of the ash sluicing system arising from CO_2 transfer between the process liquor and the atmosphere. The results from these cases plus the results of the two base cases previously discussed are summarized in Table 3-9.

Two additional cases for once-through sluicing operation were run: (1) allowing the process liquor in the pond to be in equilibrium with the atmosphere with respect to CO_2 and (2) allowing CO_2 equilibrium with the atmosphere in the sluice

TABLE 3-9. EFFECTS OF CO_2 MASS TRANSFER IN COMANCHE ASH SLUICING*

	Once-Through Sluicing			Recirculating Sluicing			
	Base Case	Case 2	Case 3	Base Case*	Case 2	Case 3	Case 4
CO_2 Equilibrium in Pond	No	Yes	---	No	Yes	No	Yes
CO_2 Equilibrium in Tank	No	No	Yes	No	No	Yes	Yes
Fly Ash Slurry Relative Saturations **							
$CaCO_3$	5.37	5.37	4,047.0	6.46	13.9	4,207.0	3,961.0
$CaSO_4 \cdot 2H_2O$	1.24	1.24	1.25	1.68	1.74	1.54	1.61
$Mg(OH)_2$	35,360.0	35,360.0	.045	43,010.0	45,520.0	.049	.056
Slurry pH	12.3	12.3	9.5	12.7	12.7	9.5	9.5
Pond Overflow pH	12.7	12.7	---	12.7	8.0	---	---

* Pond desupersaturation of $CaSO_4 \cdot 2H_2O$ allowed.

** Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$, about 2.5 for $CaCO_3$, and about 3.4 for $Mg(OH)_2$ (see Appendix C) tank. Allowing CO_2 equilibrium in the ash pond has no effect on the fly ash slurry, but this reduces the ash pond overflow pH to 7.9 from the base case value of 12.7. Carbon dioxide equilibration in the sluice tank results in an increase in scale potential for $CaCO_3$ and completely eliminates $Mg(OH)_2$ scale potential. In any event, the $CaCO_3$ relative saturation remains above the critical level of 2.5 which may cause scaling problems. The gypsum relative saturation remained virtually unchanged by the CO_2 equilibration.

Three additional cases were run for the recirculating ash sluicing system using cooling tower blowdown to sluice fly ash and ash pond recycle to sluice bottom ash. These were (1) CO_2 equilibrium in the pond only, (2) CO_2 equilibrium in the tank only, and (3) CO_2 equilibrium for both the pond and tank. Case 2 for this system in Table 3-9 indicates that CO_2 equilibration between the atmosphere and the pond increases the $CaCO_3$ scale potential (relative saturation increased from 6.46 to 13.9) and increases the $Mg(OH)_2$ scale potential (relative saturation increased from 43,010 to 45,520). The $CaSO_4 \cdot 2H_2O$ relative saturation increased slightly, from 1.68 to 1.74.

Case 3 for this system, representing CO_2 equilibrium with the atmosphere in the sluice tank but no CO_2 transfer in the pond, indicates that the $CaCO_3$ scaling potential is drastically increased, but the $Mg(OH)_2$ scaling potential is greatly reduced. The gypsum scaling potential is decreased but still remains above its critical scaling level. The decrease was due to the increased amount of calcium associated with carbonate ions in solution, which lowers the calcium ion activity. The great decrease in $Mg(OH)_2$ relative saturation is attributable to the lowering of the pH between the base case and Case 3.

Case 4 represents operation where CO_2 equilibrium is achieved in both the ash pond and the sluice tank. In this case the $CaCO_3$ relative saturation is greater than that of the base case, while the $Mg(OH)_2$ relative saturation is greatly reduced. The gypsum relative saturation is only slightly changed between Case 4 and the base case (1.61 versus 1.68).

Preventing gypsum scaling is the most important consideration in the ash sluice system due to the difficulty of removing the scale, and Case 3 is the most favorable case on this basis. However, all four cases have $CaSO_4 \cdot 2H_2O$ relative saturations exceeding the critical scaling level, and all will require some form of treatment to prevent gypsum scale potential.

3.3 Conclusions

From the results of the cooling tower and ash sluice system simulations discussed in the previous sections, two alternatives for reducing plant discharges with fly ash sluicing in the system are considered technically feasible. These are:

1) Cooling system operation at 5.0 cycles of concentration (existing operations) with once-through ash sluicing for both fly ash and bottom ash. The ash pond overflow can be discharged after pH adjustment or can be treated with a brine concentrator/reverse osmosis unit, with the clean water recycled to the boiler and cooling tower makeup systems.

2) Cooling system operation at 7.6 cycles of concentration with the sluicing of bottom ash accomplished by using recycled ash pond water. The fly ash will be sluiced with cooling tower blowdown which has been treated to remove calcium and sulfate, and recycled pond water.

Another alternative exists in which fly ash disposal is effected by dry methods, as is currently done at Comanche. The cooling towers may be operated at 8.4 cycles of concentration (with treatment for silica removal if necessary) providing 16.4 ℓ/sec (260 GPM) blowdown for boiler refractory cooling for each unit. This water may then be used to sluice bottom ash on a recirculating basis at about 1% solids, resulting in an ash pond overflow of about 15.1 ℓ/sec (240 GPM) per unit. About 58.4 ℓ/sec (930 GPM) of pond overflow is recycled in this system. Zero discharge may be achieved with this alternative by treating the overflow by brine concentration and recycling the clean water to the boiler and cooling tower makeup systems.

The first alternative may necessitate the use of reaction tanks before the fly ash sluice line to minimize $CaCO_3$ and $Mg(OH)_2$ scale formation in the line. Adjustment of the pH of the ash pond overflow may be required, depending on the amount of CO_2 transfer occurring in the ash pond. The calculated pH for equilibrium with respect to CO_2 between the pond and the atmosphere is 7.9, but the value for no CO_2 transfer is 12.7.

The second alternative will also include reaction tanks in the fly ash sluice system, as in the first alternative. In addition, recycle lines and pumps will be required to return a portion of the ash pond liquor for sluicing. This alternative involves operating the cooling towers at 7.6 cycles of concentration, which may possibly result in scale in the condenser due to silica. Chemical studies will need to be undertaken to investigate whether scaling will occur. If scaling will occur at this increased level of concentration, it will be necessary to lower silicate concentrations in the cooling tower makeup water. This can be accomplished by using hot lime-soda ash softening (RO-266) or the magnesium bicarbonate process (TH-192) for the makeup water instead of just lime treatment. Approximately 50% of the cooling tower blowdown must be treated to remove calcium and sulfate to avoid gypsum scaling in the sluice line. The cost estimates presented in the next section are based on brine concentration used for this treatment step.

The second alternative can achieve zero-discharge by treatment of the ash pond overflow with a brine concentrator/ reverse osmosis unit. Discharge of the ash pond overflow may require pH adjustment as in the first alternative, depending on the amount of CO_2 transfer in the pond.

The third alternative should not require pH adjustment of the ash pond overflow before discharge because of the insoluble nature of the bottom ash.

It should be emphasized here that none of the alternatives should be implemented before more information is gathered from a bench or pilot scale test program to determine (1) the actual size of reaction tank required in the sluice system, (2) the quantity and frequency of acid wash water required to minimize $CaCO_3$ and $Mg(OH)_2$ scale formation, and (3) the solubility limits for silica in the cooling tower system.

An economic analysis based on rough cost estimates for these alternatives is given in the following section.

4.0 ECONOMICS

This section provides rough cost estimates for the technical alternatives discussed in Section 3.0. Both capital costs and operating costs are given. These costs should be considered to be rough estimates for comparative purposes. The assumptions used in making these estimates are outlined below.

A capital cost summary for the two technically feasible alternatives employing wet fly ash disposal and the third alternative (dry fly ash disposal) is presented in Table 4-1. The fly ash slurry tanks were sized based on a five minute residence time to permit most of the soluble ash species to be leached in the tank. The tanks are general storage tanks equipped with wear liners. One tank was used for each of the two Comanche units and was assumed to have one agitator to keep the slurry well mixed. Pumps and piping sizes were based on the flows used in the simulations discussed in Section 3.0. Eight-inch carbon steel buried pipe with average fittings, flanges, shop coating, and wrapping was assumed for fly ash sluice lines. Four-inch pipe was used for the fly ash recycle line. A labor-to-material ratio was used for the fly ash recycle installation costs. Engineering costs (direct and indirect) were assumed to be 7.2% of the combined labor and material cost (GU-075).

Cast steel pumps with electric motor drivers were used for all streams. The fly ash slurry pumps were lined with neoprene for wear resistance, a labor-to-material ratio of 0.36 was used for installation costs. Engineering was assumed to be 10% of the combined labor and material cost (GU-075). All pump and piping costs were upgraded from 1970 dollars to 1976 dollars using a factor of 1.56 (based on Chemical Engineering Index).

The operating cost for the once-through system, assuming 2¢/kW-hr and 15% per year for capital cost amortization, totals $90,000/yr (1976 dollars). The recirculating sluice system will cost about $863,000/yr, of which $549,000 is for capital cost amortization, $53,000 is for pump and agitator power consumption, and the remainder is for brine concentration. If additional treatment is necessary to prevent silica scale in the condenser, the cost of this treatment will be an additional operating cost. Also, if the pond overflow is discharged, an acid cost may be involved, depending on the amount of CO_2 transfer in the ash pond and the resultant pond pH. The operating costs for alternative three are about $38,000/yr, $33,000/yr being for capital amortization at 15% per year.

TABLE 4-1. CAPITAL COSTS FOR WATER RECYCLE/ REUSE ALTERNATIVES AT COMANCHE

	Alternative One (1976 dollars)	Alternative Two (1976 dollars)	Alternative Three (1976 dollars)
Fly Ash Slurry Tanks*	29,000	29,000	---
Agitators	9,000	9,000	---
Ash Slurry Pumps and Drivers	87,000	87,000	---
Ash Sluice Piping	157,000	157,000	---
Pond Recycle Pumps and Drivers	---	39,000	24,000
Pond Recycle Piping	---	263,000	157,000
Brine Concentration**	---	2,400,000	---
Contingency (20%)	52,000	590,000	36,000
Contractural Fees (3%)	8,000	88,000	5,000
TOTAL	342,000	3,662,000	222,000

*Includes wear liner and agitator supports.

**$7750/GPM

References: GU-075, LE-239, MC-136

TABLE 4-2. CAPITAL AND OPERATING COSTS FOR ATTAINING ZERO DISCHARGE AT COMANCHE

	Alternative One		Alternative Two		Alternative Three	
	Capital Cost[1]	Operating Cost[2]	Capital Cost[1]	Operating Cost[2]	Capital Cost[1]	Operating Cost[2]
Softening/R.O./Brine Concentration[3]	8,107	2,096	3,550	917	3,720	962
Additional Pumps	17	17	12	5	13	5
Additional Piping	156	23	144	22	150	22
Total Additional Cost	8,280	2,136	3,706	944	3,883	989
Costs from Table 4-1	342	90	3,662	863	222	38
Total Overall Cost for Zero Discharge (mils/kW-hr)	8,622	2,226 (0.45)	7,368	1,807 (0.37)	4,105	1,027 (0.21)

[1] 1976 $ x 10^{-3}

[2] 1976 $ x 10^{-3}, including capital cost amortization at 15% for a 30-year lifetime, based on 80% load factor

[3] Capital Cost = $7750/GPM feed (LE-239)
Operating Cost = $2/1000 gal (not including capital cost amortization)

Additional capital and operating costs for treating the ash pond overflow so that it may be recycled to achieve zero discharge are presented in Table 4-2. The overflows can be treated by a combination of softening, reverse osmosis, and brine concentration. The clean water can then be recycled to the plant boiler and cooling tower makeup systems. For the once-through system, about 32.7 ℓ/sec (518 GPM) must be treated per unit. For the recirculating system, 14.4 ℓ/sec (229 GPM) must be treated per unit. For dry fly ash disposal, about 15.1 ℓ/sec (240 GPM) of ash pond overflow from each unit must be treated to achieve zero discharge at the plant.

The third alternative for achieving zero discharge is the least expensive since no intermediate treatment to prevent gypsum scaling is required. The second alternative (recirculating fly ash sluice system) produces an ash pond overflow of about the same magnitude as the third alternative but requires treatment of the cooling tower blowdown to remove calcium and sulfate.

The once-through sluicing of fly ash and bottom ash is less expensive than the recirculating system if zero discharge is not desired because no treatment is involved. However, to achieve zero discharge with the once-through system requires treatment of a much larger stream than in the recirculating system. This makes the once-through alternative more expensive.

Appendix I. Recycle/Reuse Options at Montour (Pa. Power and Light Co.)

1.0 INTRODUCTION

This appendix describes the analysis of the water system at Pennsylvania Power and Light Co.'s (PP&L) Montour plant, under EPA Contract No. 68-03-2339, Water Recycle/Reuse Alternatives in Coal-Fired Power Plants. This section presents a summary of the important results of the study at Montour. The major water systems at the two-unit, 1500 Mw Montour plant are the natural draft cooling tower and once-through ash sluicing systems. Montour was selected with four other plants for evaluation of the technical and economic feasibility of various water recycle/reuse alternatives.

Three major topics are addressed in this study:

1) Existing Operations Modeling

2) Alternatives Modeling

3) Economics

The results of the existing operations simulations of the cooling towers compare well to the sample data obtained at the plant. The calculated $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ relative saturations in the cooling tower water (0.02-0.04 and 0.02-0.03, respectively) indicate that the cycles of concentration may be significantly increased without calcium sulfate (gypsum) scale. However, a substantial increase in cycles of concentration will probably require treatment such as acid addition to control calcium carbonate scale.

Eight cooling tower simulations were performed to determine the degree of acid treatment necessary for increased cycles of concentration in the towers (to reduce cooling tower blowdown) and the effects of different magnesium levels in the makeup water. Magnesium was chosen to be studied since the effects of calcium and sulfate were identified at other plants. Magnesium is an important species due to the numerous complexes formed and can have significant effects on operation. No scale potential for $CaSO_4 \cdot 2H_2O$ was identified in any of the cases. Sulfuric acid treatment was required for $CaCO_3$ scale control in all cases at or above 8 cycles of concentration. Increased magnesium levels reduced the scale potential of $CaCO_3$ and therefore reduced the amount of sulfuric acid required to prevent $CaCO_3$ scale formation. No scale potential was found for any phosphate or silicate solids even at 20 cycles of concentration, which is the highest cycles of concentration considered.

Table 1-1 presents a summary of the technically feasible options for the Montour water system as compared to existing operations and the relative costs of each of these alternatives. Four process alternatives were studied for the water systems at Montour. All alternatives sluiced bottom ash and fly ash at 5 wt. % solids. Mill rejects were sluiced at 0.5% solids. In all cases ash pond liquor was recycled to the ash sluicing operation. In one case, Alternative 4, a blowdown was taken from the system to prevent $CaSO_4 \cdot 2H_2O$ scale. The other three alternatives did not discharge any liquid streams and controlled $CaSO_4 \cdot 2H_2O$ scale with softening of a portion of the pond recycle water. It should be noted here that this analysis was performed to study general water recycle/reuse alternatives. Actual implementation of any of these alternatives would require a more extensive investigation of process parameter variability. More water quality data would be required along with additional studies to fully characterize the ash leachability as a function of time.

Potential scaling of $CaCO_3$ is present in all four cases. However, the fly ash slurry line possibly can be kept free of plugging by the addition of a fly ash slurry reaction tank and/or by flushing with acidic water. Pilot or bench scale testing is recommended to determine accurately the size of reaction tank and frequency and quantity of acid washing required or if other measures are necessary.

For each alternative the effect of CO_2 mass transfer in both the pond and the sluice tank was studied. It was found that CO_2 equilibrium in both the tank and the pond decreased the pH and thus the scale potential for $CaCO_3$ and $Mg(OH)_2$. CO_2 transfer did not significantly affect $CaSO_4 \cdot 2H_2O$ scale potential.

The first alternative assumes that the cooling tower drift from one tower was equal to the design value of 32 ℓ/sec (500 GPM). Enough blowdown was drawn from the cooling towers to serve as makeup to the recirculating sluicing operation. Under this situation the cooling tower should be operating near 8 cycles of concentration.

The second alternative is identical to Alternative 1 except that the cooling tower drift was assumed to be negligible. This assumption increased the cycles of concentration from 8 to 20 even though the blowdown rate was not changed. This had the effect of requiring more softening for the pond recycle stream because of the poorer quality of makeup water to the ash sluicing operations.

TABLE 1-1. SUMMARY OF TECHNICALLY FEASIBLE OPTIONS AT MONTOUR

	Existing Condition	Alternative 1	Alternative 2	Alternative 3	Alternative 4
Cycles of Concentration in Cooling Towers	1.5 - 2.0	8	20	20	20
Assumed Drift Rate in Cooling Towers ℓ/sec (GPM)	62 (1,000)	62 (1,000)	0	40 (650)	40 (650)
Blowdown from Cooling Towers ℓ/sec (GPM)	725 (11,500)	48 (760)	40 (650)	0	0
% Recycle in Fly Ash Sluicing System	0	89.	89.	89.	73.
Sluice System Makeup Source	Cooling Tower Blowdown	Cooling Tower Blowdown	Cooling Tower Blowdown	River Water	River Water
Total Makeup Water Rate, ℓ/sec (GPM)	1,500 (24,000)	1,000 (16,000)	950 (15,000)	985 (15,600)	1,035 (16,400)
Ultimate Effluent Rate, ℓ/sec (GPM)	500 (7,900)	0	0	0	50 (800)
Treatment Required	None	H_2SO_4 (Cooling Tower)[1] Na_2CO_3 (Pond Recycle)	H_2SO_4 (Cooling Tower)[1] Na_2CO_3 (Pond Recycle)	H_2SO_4 (Cooling Tower)[1] Na_2CO_3 (Pond Recycle)	H_2SO_4 (Cooling Tower)[1]
Costs[3]					
Capital, 1976 $	--	640,000	668,000	622,000	485,000
Operating, 1976 $/yr[4]	--	173,000	187,000	169,000	103,000
(mils/kW-hr)		(0.016)	(0.018)	(0.016)	(0.010)

[1] Sulfuric acid treatment for $CaCO_3$ scale control

[2] Na_2CO_3 softening for Ca removal

[3] These rough cost estimates were made to compare technically feasible options and do not include a "difficulty to retrofit" factor.

[4] Includes capital amortization of 15% per year.

The other two alternatives assume that the cooling towers can be operated at zero blowdown. This requires that the drift be at least 65% of the design value. Under these alternatives the makeup water to the ash sluicing operation is obtained directly from the Susquehanna River or the plant makeup pond. Alternative 3 employed softening and attained zero discharge similar to the two previous alternatives. Alternative 4 controlled the $CaSO_4 \cdot 2H_2O$ scaling potential by the use of a blowdown stream of about 50 ℓ/sec (800 GPM) from the ash pond (both units).

Rough cost estimates for the different alternatives are also presented in Table 1-1. Alternative 4 is the least expensive due to the fact that no softening was required. The other three vary mostly in the degree of softening that was required for the recirculating ash sluicing system. It should be emphasized that Alternatives 1 and 2 differ only in the assumption concerning the drift rate in the cooling towers. If more information could be obtained about the actual drift rate, a more reliable cost estimate could be made.

Detailed discussions of the existing operations simulations, the alternative simulations, and the rough cost estimates constitute the main body of this appendix.

2.0 PLANT CHARACTERISTICS

The Pennsylvania Power and Light (PP&L) Montour Station consists of two 750 Mw coal-fired units located near Washingtonville, Pennsylvania. The coal used at Montour is supplied by three different mines: Oneida, Rushton, and Greenwich. The Greenwich mine accounts for more than 80% of the coal burned at Montour. Typical Greenwich coal is approximately 20% ash and 2% sulfur with a heating value of about 12,000 Btu/lb. The plant has two large natural draft cooling towers and uses once-through sluicing for fly ash, bottom ash, and mill reject disposal.

This section of the appendix describes the characterization of Montour's water system. First, an overall plant water balance is presented which shows the major in-plant flows and chemical analyses for the streams which were sampled. Then a detailed description of each of the major water consumers in the plant is given. This is followed by a discussion of the process model and the input data used to simulate existing operations at Montour. The computer simulation results are finally presented and discussed. This discussion includes a comparison of the simulation results and the chemical analyses of the samples taken. Areas which show a potential for water recycle/reuse at Montour are identified and discussed.

2.1 Water Balance

A flow schematic for the Montour water system is shown in Figure 2-1. The major streams in the plant, including the cooling tower and ash handling systems, are shown in this diagram. The numbers in the diamonds refer to the stream numbers shown with the design flows and results of the chemical analyses of the samples taken at Montour. A more detailed description of the samples taken and analytical procedures used is presented in Appendix B.

The composition of the makeup water is consistent with data obtained from PP&L about the water quality of the Susquehanna River from January, 1974 until December, 1976. The concentrations of the key species used in this study (Ca, Mg, Na, K, Cl, SO_4, and NO_3 as well as TDS and pH) were all in the range of values found over this three year period. The silicate and the phosphate concentrations found in the samples were smaller than those found in the data supplied by PP&L.

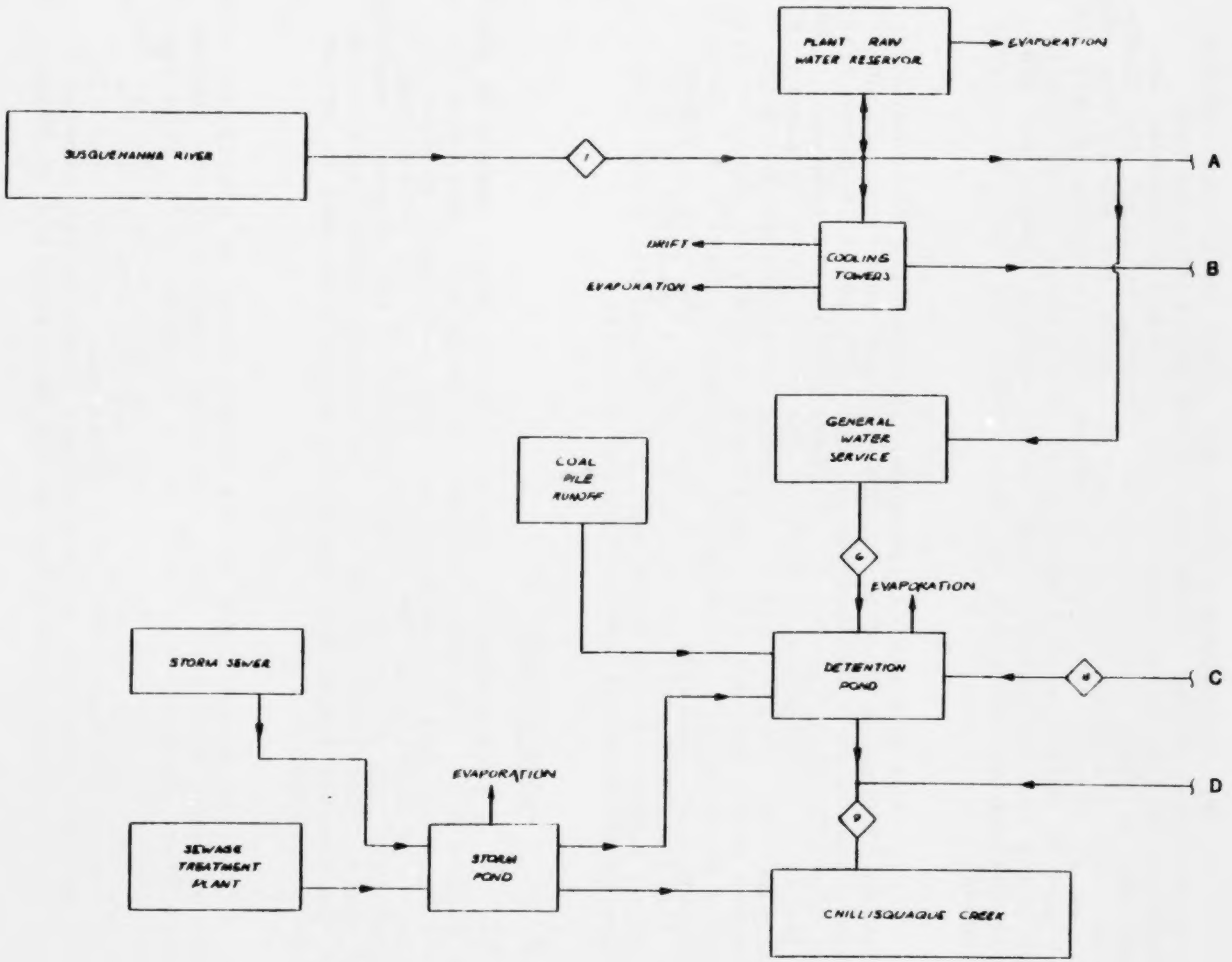


Figure 2-1. Pennsylvania Power and Light Company Montour Plant Water Balance.

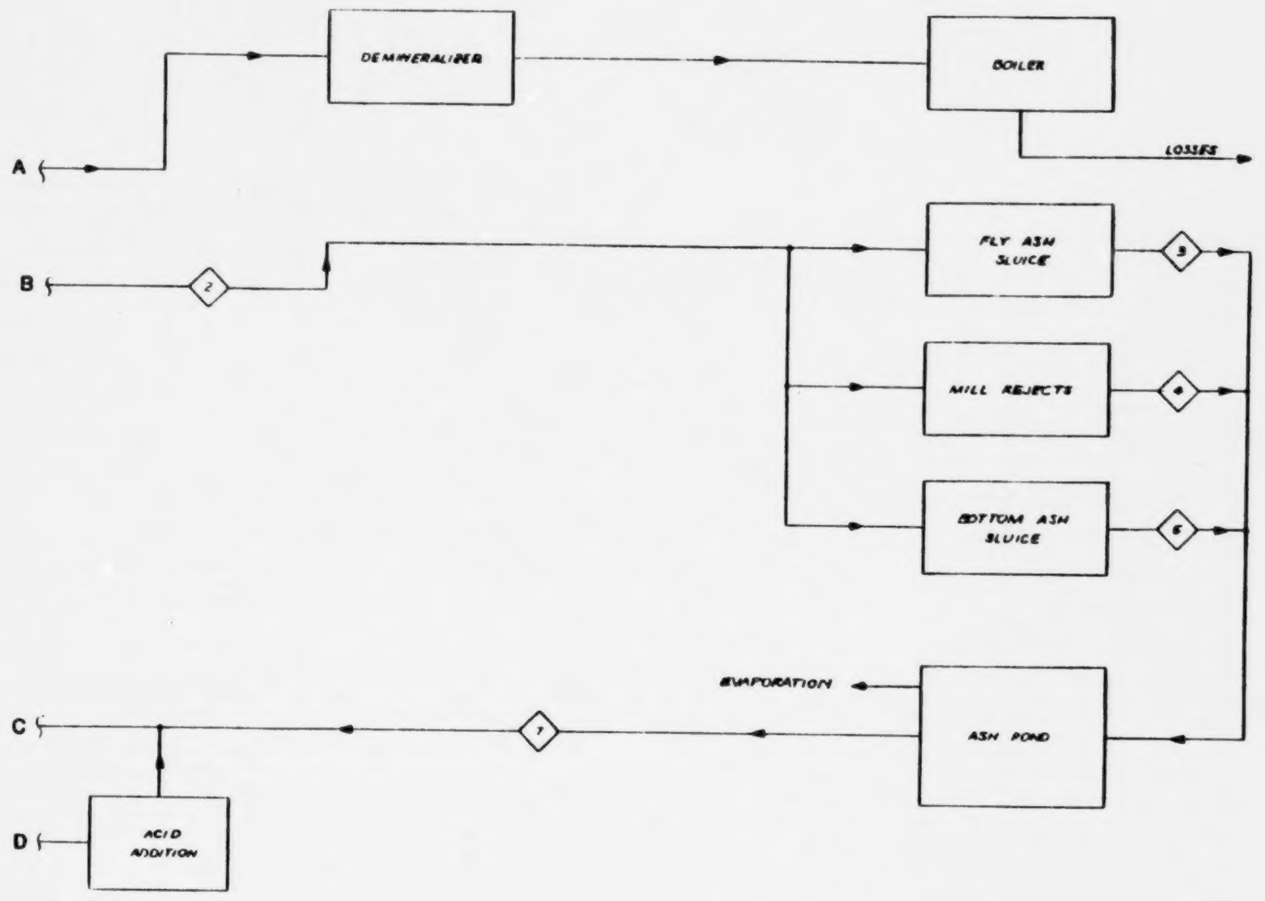


Figure 2-1. (Continued)

Stream Number	1	2	3	4	5	6	7	8	9
Stream Name	Cooling Tower Makeup	Cooling Tower Blowdown*	Fly Ash Slurry	Mill Reject Slurry**	Bottom Ash Slurry**	Misc. Waste	Ash Basin	Ash Basin Overflow	Detention Basin Overflow
Flow: Metric English	1,500 ℓ/sec. 24,000 gpm	450 ℓ/sec. 7,400 gpm	300 ℓ/sec. 4,800 gpm	80 ℓ/sec. 1,200 gpm	120 ℓ/sec. 1,900 gpm	90 ℓ/sec. 1,400 gpm	500 ℓ/sec. 7,900 gpm	500 ℓ/sec. 7,900 gpm	590 ℓ/sec. 9,300 gpm
pH	8.1	7.5	8.9	6.9	5.8	7.7	8.7	7.7	7.5
Calcium	28.4	46.5	142.0	39.9	39.4	28.4	98.9	98.9	87.4
Magnesium	5.5	11.1	10.4	11.7	9.0	6.0	10.0	10.0	9.0
Sodium	7.0	10.2	12.6	9.4	9.8	7.4	11.4	11.8	19.1
Potassium	2.6	3.0	9.9	4.2	5.0	0.9	8.2	7.4	6.6
Chloride	19	33	38	33	32	18	33	34	29
Carbonate (as CO_3)	6.0	9.3	3.8	7.8	35.4	10.8	24	9.6	1.5
Sulfate (as SO_4)	66	110	267	78	101	66	197	245	215
Nitrate (as NO_3)	5.5	11.0	13.3	11.8	11.5	5.5	6.8	9.9	11.1
Phosphate (as PO_4)	.029		.224		.040			1.02	.056
Silicates (as SiO_3)	0.9	2.5	2.1	0.5	2.0	0.6	1.4	2.0	1.4
Arsenic		<.02	.067						
Suspended Solids	.0008	.0004	2.1	.0056	.0532	.0016	.004	.0012	.0016
Dissolved Solids	100	235	690	190	200	170	470	460	290

*Average of the values found from each cooling tower.

**Normalized to continuous operation. Actual flows are intermittent.

Figure 2-1. (Continued)

Makeup water for the plant is taken from the Susquehanna River and can be stored in a raw water reservoir. Water is supplied to the system at a design rate of 1500 ℓ/sec (24,000 GPM) and is used as general service water, boiler makeup, and cooling tower makeup.

Miscellaneous plant wastes total about 90 ℓ/sec (1,400 GPM) and are sent to a detention basin before ultimate discharge. The major water consumers at the Montour plant are the cooling tower system and the ash handling systems, which are discussed in the following sections.

The first step in analyzing the water systems at Montour is to examine the results of the grab samples obtained at Montour. Parameters calculated by the equilibrium program for the streams sampled are presented in Table 2-1. Included are the relative saturations of $CaCO_3$, $CaSO_4$, and $Mg(OH)_2$ as well as the equilibrium partial pressure of CO_2 and the % residual electroneutrality. These parameters are useful for characterization of the individual streams.

The relative saturation is a parameter which indicates the potential of a stream to produce scale. When the relative saturation is greater than the critical value, solids formation is likely. The critical values for the three species reported in Table 2-1 are 2.5 for $CaCO_3$, 3.4 for $Mg(OH)_2$, and 1.3-1.4 for $CaSO_4 \cdot 2H_2O$. From the values in the table no scale potential is calculated for any stream except for the fly ash sluice and the ash pond, where $CaCO_3$ relative saturations are 6.8 and 8.1, respectively.

The equilibrium partial pressure of CO_2 for each of the streams sampled at Montour is also presented in Table 2-1. The partial pressure of CO_2 in air is about 3.3×10^{-4} atm. Most of the streams have partial pressures of CO_2 near this value. The cooling tower makeup and the fly ash sluice values are significantly lower than atmsopheric indicating a tendency to absorb CO_2 and the bottom ash sluice value is higher than atmsopheric indicating a tendency to desorb CO_2.

The percent residual electroneutrality is the difference between the total positive charge and the total negative charge as a percent of the total charge. It is an indication of how accurately the actual stream is represented by the computer model. More information on the residual electroneutrality is presented in Appendix E. The values reported in

TABLE 2-1. PARAMETERS CALCULATED BY THE EQUILIBRIUM PROGRAM FOR MONTOUR SAMPLES

Stream Name	Stream No.	Relative Saturations*			Equilibrium Partial Pressure of CO_2 atm	% Residual Electroneutrality
		$CaCO_3$	$Mg(OH)_2$	$CaSO_4 \cdot 2H_2O$		
Cooling Tower Makeup	1	.013	5.45×10^{-7}	.012	3.95×10^{-5}	4.1
Cooling Tower Blowdown	2	.031	2.34×10^{-6}	.023	2.84×10^{-4}	4.7
Fly Ash Sluice	3	6.83	2.49×10^{-3}	.105	3.18×10^{-5}	11.3
Mill Rejects	4	2.94×10^{-3}	4.79×10^{-8}	.015	6.96×10^{-4}	12.1
Bottom Ash Sluice	5	3.84×10^{-4}	5.40×10^{-18}	.019	1.13×10^{-2}	1.2
Miscellaneous Wastes	6	.014	2.82×10^{-7}	.011	1.78×10^{-4}	3.2
Ash Basin	7	8.08	3.86×10^{-5}	.066	3.74×10^{-4}	-18.9
Ash Basin Overflow (Acidified)	8	.024	1.73×10^{-7}	.093	1.46×10^{-4}	2.4
Detention Pond Overflow	9	.021	6.36×10^{-8}	.076	3.54×10^{-4}	5.3

*Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$, about 2.5 for $CaCO_3$, and about 3.4 for $Mg(OH)_2$ (see Appendix C)

Table 2-1 are generally quite good and tend to confirm the accuracy of the analyses.

2.2 Cooling Tower System

Each of the two 750 Mw units has an independent cooling system. Water circulates between each tower and condenser at a rate of about 16,000 ℓ/sec (250,000 GPM). The blowdown is removed from the system before the condenser. Water from either the river or the raw water reservoir or both is added to the system as makeup to replace water lost through evaporation, drift, and blowdown.

The towers normally operate at 1.5 - 2.0 cycles of concentration, which may be defined as the ratio of blowdown species concentrations to makeup species concentrations. In terms of flow rates, cycles of concentration is defined as:

$$C = \frac{E + B + D}{B + D}$$

where C = cycles of concentration
E = evaporation rate
B = blowdown rate
D = drift rate

2.2.1 Simulation Basis

The existing operations of the Montour cooling towers were simulated by means of the computer model shown in Figure 2-2. This was done in order to verify the validity of this model and to establish a sound basis from which potential recycle/reuse options could be compared. The model used information concerning the inlet air flow and composition, the makeup water composition, the recirculating water flow rate, the drift rate, the desired cycles of concentration, and the temperature change across the condenser as inputs. From these inputs the heat load on the condenser, and the flows and compositions of all the streams in Figure 2-2 are calculated. A detailed description of the cooling tower model including a brief discussion of the subroutines in Figures 2-2 is presented in Appendix E.

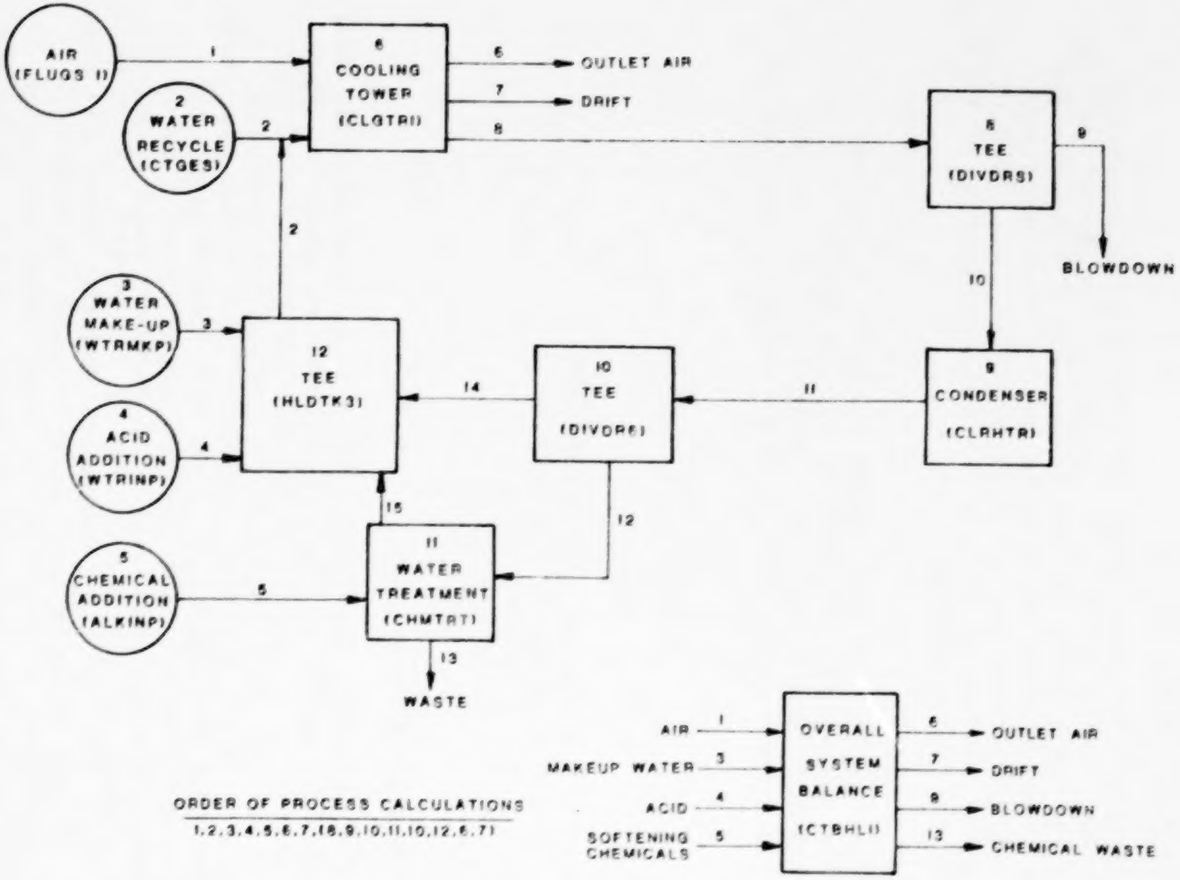


Figure 2-2. Process simulation scheme for Montour cooling tower system.

02-1169-1

Several assumptions were made in modeling the cooling towers with this simulation. These include:

1) Equilibrium exists between CO_2 and H_2O in the atmosphere and cooling tower exit water.
2) The temperature of the cooled water stream approaches the wet bulb temperature of ambient air within a predictable range.
3) The compositions and temperatures of the cooled water and drift streams are equal.
4) Ionic reactions taking place in the liquid phase are rapid and thus at equilibrium.

The assumption involving the temperature of the cooled water stream is a recognized design parameter in cooling tower evaluation and gives a good approximation. The assumption concerning the temperature and composition of the drift stream should be very close to actuality as is the assumption in regard to H_2O gas-liquid equilibrium. The assumption with regard to CO_2 equilibrium is conservative since the partial pressure of CO_2 in actual cooling towers tends to be slightly greater than the equilibrium value. The lower equilibrium concentration of carbonate species, assumed in the model, causes the pH to be slightly higher in the model than in actual operation. The higher pH causes the relative saturation of $CaCO_3$ to increase more than the lowered carbonate species concentration causes it to decrease.

A summary of the input stream data employed in the existing operations simulations is presented in Table 2-2. The air temperature and composition were calculated using local climatological data for Williamsport between December, 1975 and August, 1976. The makeup water composition was obtained from chemical analyses of the spot sample taken in November, 1976.

The cooling tower drift rate, approach, cycles of concentration, and circulating water flow were obtained directly from PP&L or calculated from data obtained from PP&L. The condenser temperature change was also obtained from PP&L. The

TABLE 2-2. INPUT DATA FOR MONTOUR COOLING TOWER SIMULATIONS

	December 1975	August 1976
FLOWS		
Air, m^3/hr	3.5×10^7	3.5×10^7
(ACFM)	(2.06×10^7)	(2.06×10^7)
Drift, ℓ/sec	31.5	31.5
(GPM)	(500)	(500)
Circulating Water, ℓ/sec	14,600	18,700
(GPM)	(232,000)	(296,000)
TEMPERATURES		
Ambient Air, °C	0	21
(°F)	(32)	(70)
Approach, °C	20	10
(°F)	(36)	(18.5)
Condenser ΔT, °C	20	16
(°F)	(36)	(28)
Wet Bulb, °C	-2	18
(°F)	(29)	(64)
Condenser Outlet, °C	36	43
(°F)	(97)	(110)
ADDITIONAL DATA		
Relative Humidity, %	72.0	72.0
Cycles of Concentration	2.0	1.5,2.0
Makeup Water Composition, mg/ℓ		
Calcium	28.4	28.4
Magnesium	5.5	5.5
Sodium	8.1	8.1
Chloride	22.0	22.0
Carbonate (as $CO_3^=$)	6.0	6.0
Sulfate (as $SO_4^=$)	67.0	67.0
Nitrate (as NO_3^-)	5.5	5.5

ambient air wet bulb temperatures were derived from Williamsport climatological data for December, 1975 to August, 1976. Examples of the calculations performed to obtain the data are presented in Appendix K.

2.2.2 Simulation Results

This section describes the results from the simulation of existing cooling tower operations at Montour. Simulations were performed using weather data from December, 1975 and August, 1976. The makeup water composition was based on that which was sampled at the plant in November, 1976, with adjustment to minimize the residual electroneutrality using the method described in Appendix E.

Samples were taken from the blowdown of both cooling towers. Table 2-3 presents the data obtained from both towers as well as the results of the simulations performed. Two simulations were done under summer conditions at 1.5 and 2.0 cycles, and one under winter conditions at 2.0 cycles of concentration.

The three simulations agree reasonably well with the sampled data. The pH in all three simulations is between the values found at the plant. The simulations at 2 cycles show concentrations which were slightly higher than those measured for all species except magnesium and nitrate concentrations which were between the sample values. The simulation at 1.5 cycles tended to have concentrations which were slightly lower or in between sampled values except for carbonate which was slightly higher. These discrepancies may be due to deviations from steady state during sampling, nonhomogeneous sampling and/or analytical errors.

The $CaCO_3$ relative saturations are consistent with the input data. The larger value reported under summer conditions is probably due to the small difference in pH which is caused by temperature differences. The $CaSO_4$ relative saturations agree very well with those found at the plant. In both cases low values were found indicating that the cooling towers were being run under extremely safe conditions.

In addition to relative saturations, the ACB Index is reported. This is an index developed by the Asbestos Cement Pipe Manufacturers Association and is obtained from the following expression:

TABLE 2-3. EXISTING COOLING TOWER SIMULATION RESULTS

	Plant Data		Simulations		
Cooling Tower Blowdown	Tower #1	Tower #2	December '75 2.0 Cycles	August '76 1.5 Cycles	August '76 2.0 Cycles
FLOW, ℓ/sec per tower	820*	410**	290	760	360
(GPM)	(13,000)	(6,500)	(4,600)	(12,000)	(5,700)
pH	7.8	7.3	7.5	7.5	7.6
COMPOSITION, mg/ℓ					
Calcium	43.2	49.7	56.7	42.5	56.7
Magnesium	9.5	12.6	11.0	8.2	11.0
Sodium	12.2	11.7	16.1	12.1	16.1
Chloride	32.0	33.0	44.0	33.0	44.0
Sulfate (as $SO_4^=$)	88.0	131.0	135.0	100.0	135.0
Carbonate (as $CO_3^=$)	9.6	9.0	13.1	10.9	12.8
Nitrate (as NO_3^-)	11.8	10.2	11.0	8.2	11.0
RELATIVE SATURATIONS***					
$CaCO_3$	.037	.025	.030	.042	.073
$CaSO_4 \cdot 2H_2O$	.019	.027	.033	.020	.031
ACB Index	11.0	10.6	11.0	10.8	11.1
PARTIAL PRESSURE CO_2, atm	1.32×10^{-4}	4.36×10^{-4}	3.3×10^{-4}	3.3×10^{-4}	3.3×10^{-4}

*based on design evaporation and drift rates and 1.5 cycles of concentration

**based on design evaporation and drift rates and 2.0 cycles of concentration

***critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C)

$$ACB = pH + \log (\text{Calcium} \times \text{Alkalinity})$$

This index gives information concerning the potential for corrosion of the type of fill used in the cooling towers at Montour. An example calculation is presented in Appendix K. The values calculated for the simulated runs compare very well with those found in the plant.

These simulations indicate a potential for reducing water requirements and discharges for cooling towers by increasing the cycles of concentration. As the cycles are increased, an increase in the relative saturations of $CaCO_3$ and $CaSO_4$ is expected indicating an increase in the potential for scaling problems. $CaCO_3$ scale control can be achieved through acid addition for pH adjustment. As cycles are increased the ACB Index will increase which means there will be a decrease in the corrosiveness of the water.

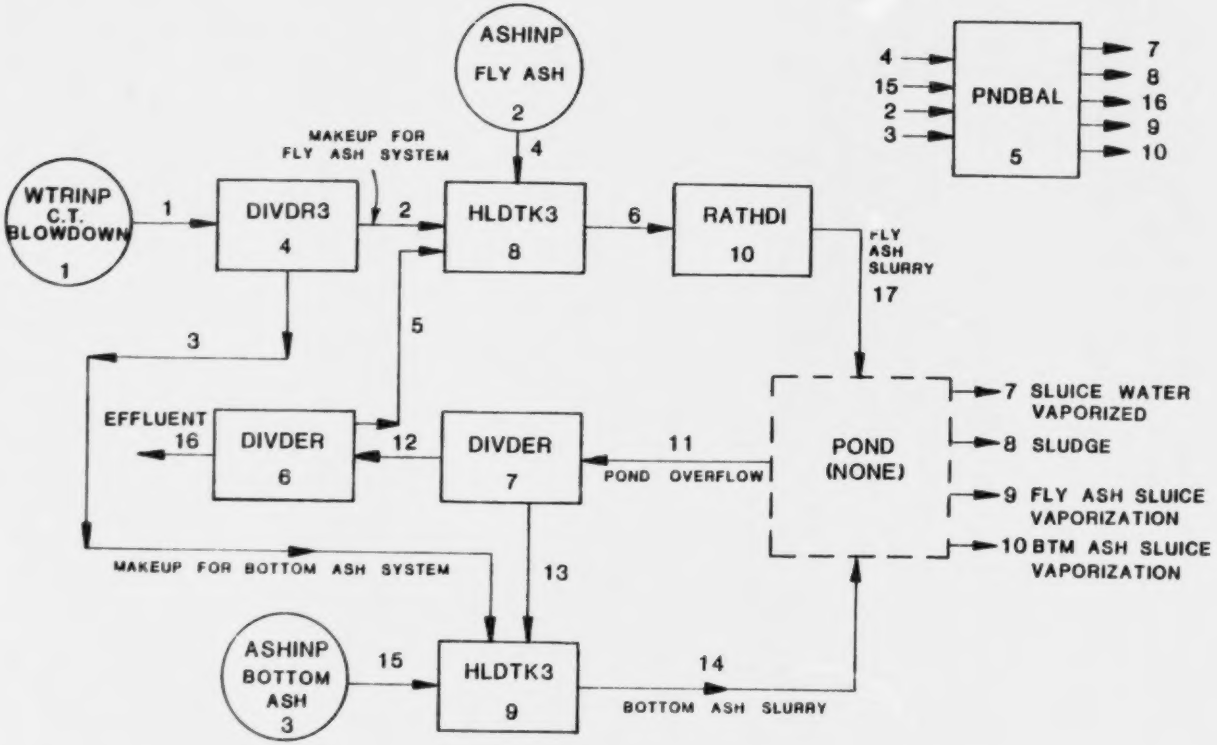
2.3 Ash Handling Systems

Fly ash is collected by each electrostatic precipitator at a rate of about 31,100 kg/hr (68,400 lb/hr) from each unit. The fly ash is sluiced on a once-through basis to the ash pond using cooling tower blowdown as sluice water. The ash is slurried at about 5% solids using 145 ℓ/sec (2400 GPM) of cooling tower blowdown.

Bottom ash and mill rejects are periodically sluiced on a once-through basis also. The amount of water needed for sluicing determines the rate at which blowdown is taken from the cooling towers.

2.3.1 Simulation Basis

The existing operations of the Montour ash sluicing system were simulated by means of the model shown in Figure 2-3. As with the cooling tower simulations, this was done in order to verify the model and establish a basis for comparison. The model used information about the composition and flows of the makeup water and the fly and bottom ash as well as the percent solids in the sludge and pond evaporation, as inputs. From this information the flows and compositions of all the streams in Figure 2-3 were calculated. A detailed description of the ash sluicing model including a brief discussion of the subroutines in Figure 2-3 is presented in Appendix E.



ORDER OF PROCESS CALCULATION: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 *

Figure 2-3. Ash sluicing simulation model.

Several assumptions were made in modeling the ash sluicing system with this simulation. These include:

1) Ionic reactions taking place in the liquid phase are rapid and thus at equilibrium.
2) Solid-liquid equilibrium is achieved in the ash pond, with the exception of $CaSO_4$ which is allowed to remain supersaturated.
3) Ash dissolution is essentially complete before the slurry reaches the pond.
4) All solids precipitation occurs in reaction vessels or the pond.

The input data required to simulate the once-through ash sluicing system at Montour are presented in Table 2-4. The fly ash, bottom ash, and water flows were obtained from data supplied by PP&L. Typical slurries of 5% solids were modeled. The evaporation rate was calculated using average ambient conditions for wind speed, temperature, and humidity. The sluice water composition used was blowdown from the cooling towers at 1.5 cycles. Sample calculations are presented in Appendix K.

Ash leaching and bench scale recirculating ash sluicing studies were performed to obtain soluble species data. The results of these studies are presented in Appendix D.

2.3.2 Simulation Results

This section describes the results from the ash sluicing simulations of existing operations. Two simulations were performed. The first did not allow CO_2 transfer in the ash pond and the second allowed the CO_2 in the pond to come to equilibrium with the atmosphere.

Table 2-5 presents the results of these simulations. The compositions of the pond liquor and fly ash slurry sampled at the plant are compared to those predicted by the model.

The concentrations of calcium, magnesium, sodium, chloride, sulfate and nitrate are not affected by the degree of

TABLE 2-4. MONTOUR EXISTING ASH SLUICING INPUT DATA

FLOWS (per unit)	
Fly Ash, kg/min	520
(lb/min)	(1140)
Bottom Ash*, kg/min	560
(lb/min)	(1230)
Fly Ash Sluice Water, ℓ/sec	175
(GPM)	(2750)
Bottom Ash Sluice Water, ℓ/sec	185
(GPM)	(2960)
Pond Evaporation, ℓ/sec	0.6
(GPM)	(10)
SLUICE WATER COMPOSITION	
Cooling Tower Blowdown @ 1.5 cycles, mg/ℓ	
Calcium	42.5
Magnesium	8.2
Sodium	12.1
Chloride	33.0
Carbonates (as $CO_3^=$)	10.9
Sulfates (as $SO_4^=$)	8.2
Nitrates (as NO_3^-)	100.3
POND DEPOSITS (wt. % solids)	50.0
SOLUBLE FLY ASH SPECIES (wt. % solids)	
$CaSO_4$	1.025
MgO	0.008
$MgSO_4$	0.066
Na_2O	0.054

*Includes mill rejects

TABLE 2-5. MONTOUR EXISTING ASH SLUICING OPERATIONS

	Fly Ash Slurry		Pond Liquor		
	Plant Data	Model	Plant Data	Model (No CO_2 Transfer)	Model (CO_2 Equilibrium)
Composition, mg/ℓ					
Calcium	142.0	193.0	98.9	115.5	115.5
Magnesium	10.4	17.1	10.0	12.6	12.6
Sodium	18.4	12.1	16.2	12.2	12.2
Chloride	38.0	33.2	33.0	33.2	33.2
Carbonates (as $CO_3^=$)	3.8	10.9	24.0	11.3	16.3
Sulfates (as $SO_4^=$)	267.0	486.0	197.0	288.0	288.0
Nitrates (as NO_3^-)	13.3	8.2	6.8	8.2	8.2
pH	8.9	9.66	8.7	9.4	7.63
Relative Saturations *					
$CaCO_3$	6.83	8.14	8.08	3.23	0.112
$Mg(OH)_2$	2.49×10^{-3}	.090	3.0×10^{-5}	7.6×10^{-3}	2.2×10^{-6}
$CaSO_4 \cdot 2H_2O$	.105	.206	0.066	0.102	0.102
Equilibrium Partial Pressure of CO_2, atm.	3.18×10^{-5}	1.05×10^{-6}	3.74×10^{-4}	2.68×10^{-6}	3.3×10^{-4}

*Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$, about 2.5 for $CaCO_3$, and about 3.4 for $Mg(OH)_2$ (see Appendix C)

CO_2 transfer as long as no solids are allowed to form. Both magnesium and chloride simulated concentrations are very close to those found at the plant for the ash pond liquor. The sodium and nitrate values are slightly lower in the simulation and the calcium is higher. The sulfate concentration is substantially higher in the simulations than in the plant samples due to the high sulfur content of the ash which was used in the leaching studies (see Appendix D). Although this high sulfur ash is probably not typical, it should make the calculated values for the relative saturation of $CaSO_4$ higher than would ordinarily be expected. This will make any recycle/reuse options obtained from these data conservative relative to $CaSO_4$ scaling.

The pH, carbonate concentration, and the relative saturation of $CaCO_3$ were affected by the degree of CO_2 transfer. The pH in the sample was between the value found with no CO_2 transfer and the value with CO_2 equilibrium. The carbonate in the sample was greater than either simulation but it was closer to the value calculated from the simulation with CO_2 equilibrium. The relative saturation of $CaSO_4$ predicted by the simulations were higher than the sample value due to the higher sulfate concentration. The relative saturation of $CaCO_3$ was lower in the simulations than the sample value due to the lower carbonate concentrations. The relative saturation of $Mg(OH)_2$ in the simulations bound the sample value.

The high relative saturation of $CaCO_3$ in the sample and in the case of no CO_2 transfer indicates that the ash sluicing system may be forming $CaCO_3$ solids. The erosive properties of the slurried ash may be keeping the walls of the slurry line "clean" of $CaCO_3$ scale.

The results of these simulations indicate that some degree of CO_2 transfer does occur in the pond. They also verify that this model can be successfully used to simulate the ash sluicing operations at Montour.

3.0 TECHNICAL ALTERNATIVES

A modular approach to studying water recycle/reuse alternatives at Montour was used in that the major plant water systems were divided into two subsystems to form separate process simulations. One subsystem consists of the cooling tower from one plant, with associated treatment facilities (where necessary), hold tanks, and condenser. The other subsystem consists of the ash handling system. The studies for each subsystem will be discussed separately. The effects of increasing the cycles of concentration in the cooling towers and of different quality makeup water (different magnesium levels) are presented first. Then the use of cooling tower blowdown in a recirculating ash sluice system is evaluated. The effects of carbon dioxide mass transfer between the atmosphere and the pond liquor are also investigated. Magnesium was chosen as the makeup parameter to be studied since calcium and sulfate variations were studied at other plants. Magnesium is an important species because of the numerous complexes which may form.

3.1 Cooling Tower System

The existing operations simulations indicated that the cycles of concentration may be increased in the cooling towers without scaling with respect to calcium sulfate or calcium carbonate. Although calcium sulfate scaling must be controlled by calcium removal, calcium carbonate scale can be controlled by acid treatment of the circulating water. This section first presents a description of the simulation bases used, then a discussion of the results with respect to increased cycles of concentration and magnesium in the makeup water.

3.1.1 Simulation Basis

The process model used to simulate alternatives for cooling tower operation is identical to that used for existing operations (Figure 2-2). Acid treatment for calcium carbonate scale control was implemented to keep the $CaCO_3$ relative saturation between 0.8 and 1.0.

A total of eight simulations were performed for alternative cooling tower operations. Six simulations were performed with the existing makeup water quality and cycles of concentration of 2.5, 4.0, 8.0, 10.5, 14.0, and 20.0. Two other simulations were performed with magnesium concentrations of one-third and tripled, at 14.0 cycles of concentration. In order to maintain a pH near the sample value, the magnesium was "added" as

$MgCl_2$. Chloride was chosen as the counter ion because it does not complex appreciably with other ions.

All of the alternative cooling tower simulations were performed for summer operation of one tower since these conditions represent the case of maximum blowdown rates. Increased evaporation rates realized during the summer months necessitate an increase in blowdown rate over that required during the winter months to maintain a constant value for cycles of concentration.

The only changes in the input data for the first six alternative simulations are the values for cycles of concentration. The adjusted makeup water compositions used in the last two cooling tower simulations (different magnesium levels) are shown in Table 3-1, along with the composition used in the first six simulations.

3.1.2 Effect of Increased Cycles of Concentration

The simulation results from six alternative operating modes of the cooling towers are presented in Table 3-2. As expected, at higher cycles of concentration acid addition was required to control $CaCO_3$ scale potential but in no case did the $CaSO_4$ relative saturation become large enough to necessitate calcium removal.

The two simulations at 2.6 and 4.0 cycles of concentration did not require acid addition. The simulations at 8.0 and 10.5 cycles did indicate a need for acid addition. Much smaller blowdown rates were attained at the higher cycles. In order to increase the cycles of concentration to 14.0 and 20.0 the drift was reduced from its design value of 32 ℓ/sec (500 GPM). At these reduced drift rates (see Table 3-2) zero blowdown was attained without $CaSO_4$ scale.

Where acid addition was used, the relative saturation of $CaCO_3$ was kept between 0.8 and 1.0. This is well below the critical scaling value of 2.5 (see Appendix C). This was done to insure that upsets in the calcium or carbonate levels would not cause scaling.

The simulation at 20 cycles of concentration indicates that the cooling towers at Montour might be able to be operated at zero discharge. The drift in this simulation was assumed to be 35% less than the design value reported by PP&L. Since the

TABLE 3-1. ADJUSTED WATER MAKEUP COMPOSITIONS FOR INCREASED MAGNESIUM LEVELS *

	1/3 Magnesium (mg/ℓ)	Normal Magnesium (mg/ℓ)	Triple Magnesium (mg/ℓ)
Carbonates (as $CO_3^=$)	6.0	6.0	6.0
Sulfates (as $SO_4^=$)	67.0	67.0	67.0
Nitrates (as NO_3^-)	5.5	5.5	5.5
Chloride	11.3	22.0	54.1
Calcium	28.4	28.4	28.4
Magnesium	1.83	5.5	16.5
Sodium	8.1	8.1	8.1
pH	8.4	8.3	8.3

*Magnesium levels were investigated since calcium and sulfate were considered at other plants.

TABLE 3-2. SIMULATION RESULTS FOR INCREASED CYCLES OF CONCENTRATION

Cycles of Concentration	Cooling Tower Blowdown									
	Flow		Relative Saturations**		ACB Index	pH	Sulfuric Acid Rate*		Drift Rate	
	ℓ/sec	GPM	$CaCO_3$	$CaSO_4 \cdot 2H_2O$			Kg/day	lb/day	ℓ/sec	GPM
2.6	213.	3380.	.146	.046	11.39	7.69	0.	0.	32	500
4.0	98.9	1570.	.447	.086	11.94	7.87	0.	0.	32	500
8.0	24.3	386.	.953	.229	12.38	7.92	74.	162.	32	500
10.5	9.64	153.	.880	.332	12.40	7.89	112.	246.	32	500
14.0	0.	0.	.898	.479	12.45	7.77	121.	266.	30	477
20.0	0.	0.	.987	.749	12.57	7.84	145.	320.	21	326

*as 100% H_2SO_4

**Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C) air flow rate in the Montour towers remains essentially constant regardless of the season, the drift should not vary widely.

The ACB Index was developed by the Asbestos Cement Pipe Manufacturers Association in order to quantify the potential for corrosive action by the cooling water on cooling tower fill. The calculations required to compute this index are presented in Appendix K. A value below 10 indicates highly aggressive conditions, and a value above 12 indicates a non-aggressive condition. Figure 3-1 is a plot of the ACB Index as a function of cycles of concentration as found in the simulations performed for Montour. Below 4 cycles of concentration there is a steep slope, whereas above 8 cycles the slope is significantly less. Above 8 cycles pH control by H_2SO_4 addition was necessary in order to prevent $CaCO_3$ scale formation. The advantage of running these cooling towers at high cycles of concentration with acid addition is dramatically displayed in this graph. In all cases where acid is used the ACB Index indicates a non-corrosive environment.

In Table 3-3 the relative saturations of many scale forming species at 20.0 cycles of concentration are reported. Since all of these species are subsaturated at 20.0 cycles they should also remain subsaturated under less concentrated situations. The relative saturation of $CaCO_3$ and $CaSO_4$ are well below their critical scaling values of 2.5 and 1.3-1.4, respectively. The silicate with the largest relative saturation is $Mg_3Si_2O_5(OH)_4$ (serpentine) with a value of 0.259, which implies that this solid is thermodynamically unstable in this water.

3.1.3 Effect of Magnesium Concentration in the Makeup Water

In addition to the simulations performed at varying cycles of concentration, two other simulations were performed at 14 cycles and different magnesium concentrations in the makeup water. The results of these simulations are presented in Table 3-4.

The results of these simulations point out that as the concentration of magnesium increases the amount of acid required to keep the relative saturation of $CaCO_3$ between 0.8 and 1.0 decreases. Similarly increases in magnesium causes the relative saturation of $CaSO_4$ to decrease. This is easily explained in that increasing the magnesium level from 1.83 mg/ℓ to 16.5 mg/ℓ causes the activity coefficients of the calcium, carbonate, and sulfate ions to decrease. Calcium decreased from

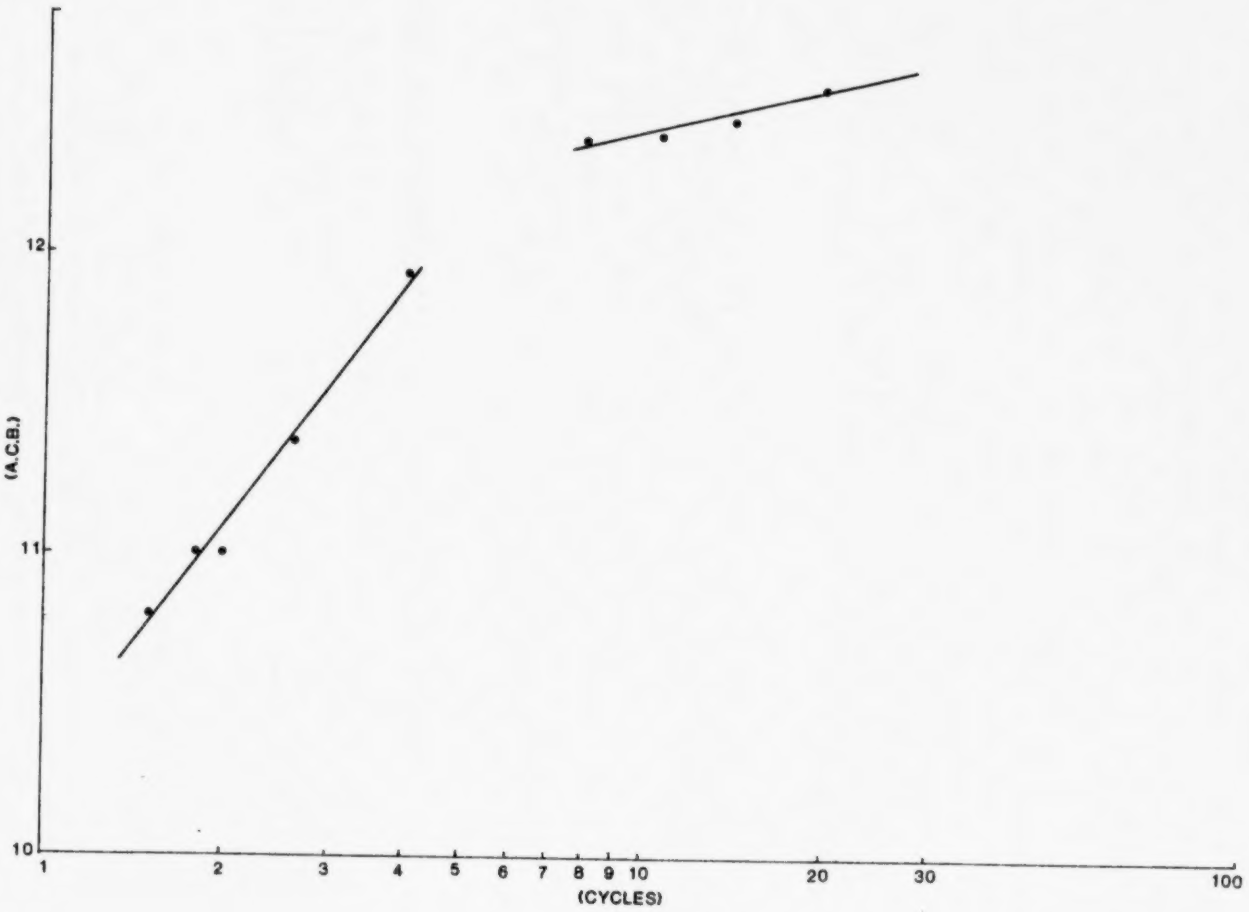


Figure 3-1. Asbestos cement pipe manufacturers index as a function of cycles of concentration.

TABLE 3-3. RELATIVE SATURATION OF SCALE FORMING SPECIES AT 20 CYCLES OF CONCENTRATION IN MONTOUR COOLING TOWERS

Solid Species	Relative Saturation
$Ca(OH)_2$	6.46×10^{-10}
$CaCO_3$	0.987
$CaSO_4 \cdot 2H_2O$	0.749
$CaHPO_4$	0.019
$Ca_3(PO_4)_2$	3.8×10^{-3}
CaH_2SiO_4	1.0×10^{-4}
$Ca(H_3SiO_4)_2$	5.0×10^{-4}
$Mg(OH)_2$	9.76×10^{-5}
$MgCO_3$	7.04×10^{-5}
$Mg_3Si_2O_5(OH)_4$	0.259
$Mg_2Si_3O_5(OH)_6$	2.49×10^{-4}
$Mg(SiO_2)_3(OH)_2$	0.031
SiO_2	0.105

TABLE 3-4. SIMULATION RESULTS WITH DIFFERENT MAGNESIUM CONCENTRATIONS (14 CYCLES)

Magnesium in the Makeup Water (mg/ℓ)	1.83	5.5	16.5
Relative Saturations*			
$CaCO_3$	0.94	0.90	0.89
$CaSO_4 \cdot 2H_2O$	0.52	0.48	0.38
$Mg(OH)_2$	3.5×10^{-5}	1.1×10^{-4}	2.0×10^{-4}
Activity Coefficients			
Ca^{++}	0.50	0.49	0.44
$CO_3^{=}$	0.49	0.48	0.43
$SO_4^{=}$	0.47	0.45	0.40
Sulfuric Acid			
kg/day	137	121	119
lb/day	301	266	261
pH	7.89	7.80	7.77

*Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$, about 2.5 for $CaCO_3$, and about 3.4 for $Mg(OH)_2$ (see Appendix C).

0.50 to 0.44, sulfate decreased from 0.47 to 0.40, and carbonate decreased from 0.49 to 0.43. The increased magnesium levels cause increased complexing between sulfate, carbonate, and magnesium which results in lower activities as well as the lowered activity coefficients. Thus, the increased presence of magnesium is seen to inhibit the scaling potential of other species.

In addition to the beneficial effects of increased magnesium there exists a potential hazard of $Mg(OH)_2$ scale. As seen in Table 3-4, the relative saturation of $Mg(OH)_2$ does increase with increasing concentrations of magnesium, but remains very low for the water quality expected at Montour.

3.1.4 Conclusions

From the results presented above, the following conclusions can be made concerning the cooling towers at Montour:

1) Sulfuric acid addition is required to control $CaCO_3$ scale when the cooling towers are operated above 4 cycles of concentration.

2) Operation of the tower with zero blowdown and design drift will cause the towers to operate near 14 cycles of concentration.

3) Cooling tower fill corrosion can be minimized if the towers are operated above 8 cycles of concentration.

4) Increased magnesium concentrations decrease the scale potential of the two important scale forming species, $CaCO_3$ and $CaSO_4$.

3.2 Ash Handling System

The existing operations simulations indicated that some recycle of the ash pond liquor to the ash sluicing operation could be accomplished without $CaSO_4$ scaling. Four alternatives using recirculating ash sluicing systems were studied. The first three alternatives attained zero discharge and used Na_2CO_3 softening to control gypsum scale. The fourth used a blowdown from the ash pond to control the gypsum scale. Different makeup water qualities were used in the first three alternatives and the fourth alternative used the same makeup water as Alternative 3.

3.2.1 Simulation Basis

The process model used to simulate alternatives for ash sluicing is identical to that used for existing operations (Figure 2-3). Because of the non-reactivity of the bottom ash it was exclusively sluiced with pond water. The more reactive fly ash was sluiced with a mixture of pond water and makeup water. Evaporation from the pond was calculated to be 1.3 ℓ/sec (20 GPM) using the empirical method shown in Appendix K.

The ash flow rates and characteristics were the same as the values used for existing operations simulations. All simulations were performed at about 5 wt. % solids. In the cases where softening was required it was assumed that a slipstream was taken from the pond recycle line and the calcium concentration was reduced to 50 mg/ℓ in this slipstream to account for treatment inefficiencies. Actual equilibrium values ranged from 22 to 29 mg/ℓ.

Table 3-5 presents the input data that was used for the alternative sluicing operations. Only that data which are different from the data used for existing operations are tabulated. The makeup water is 8 cycle cooling tower blowdown for Alternative 1, 20 cycle cooling tower blowdown for Alternative 2, and river water for Alternatives 3 and 4. Alternative 4 has a larger makeup water requirement because it has a blowdown stream.

3.2.2 Recirculating Ash Systems

The simulation results for the recirculating ash sluicing alternatives are shown in Table 3-6. Equilibrium with respect to CO_2 between the atmosphere and the ash pond was assumed. The effects of CO_2 transfer are discussed in Section 3.3.

The degree of recycle achievable in the ash sluicing system will depend upon the $CaSO_4 \cdot 2H_2O$ relative saturation in the fly ash slurry liquor since gypsum scale is of greater concern than that of $CaCO_3$ or $Mg(OH)_2$. Gypsum scale is very difficult to remove from process vessels and equipment once it is formed but $CaCO_3$ and $Mg(OH)_2$ scale most likely can be dissolved by acid washing. Both $CaCO_3$ and $Mg(OH)_2$ solubilities are pH dependent.

TABLE 3-5. RECIRCULATING ASH SLUICING INPUT DATA

Makeup Water Source	Makeup Water									% Recycle in the Fly Ash* Sluice System
	Flow		Ca^{++}	Mg^{++}	Na^{+}	Cl^{-}	$CO_3^{=}$	$NO_3^{=}$	$SO_4^{=}$	
	ℓ/sec	GPM	mg/ℓ	mg/ℓ	mg/ℓ	mg/ℓ	mg/ℓ	mg/ℓ	mg/ℓ	
Alternative 1 8 Cycle Cooling Tower Blowdown	18	291	227.	43.9	64.5	176.	30.3	43.9	555.	89
Alternative 2 20 Cycle Cooling Tower Blowdown	18	291	567.	110.	161.	440.	22.7	110.	1,430.	89
Alternative 3 River Water	18	291	28.4	5.5	8.1	22.	6.0	5.5	67.6	89
Alternative 4 River Water	44	700	28.4	5.5	8.1	22.	6.0	5.5	67.6	73

*89% recycle corresponds to zero discharge from the ash handling system. The remaining 11% of the sluice water is lost from the system by evaporation and occlusion with the solids in the pond.

TABLE 3-6. RECIRCULATING ASH SLUICING RESULTS
(CO_2 EQUILIBRIUM IN THE POND)

	Total System Makeup Water		Sluice Tank Effluent				Slipstream			Calcium Removal Rate	Blowdown	
			Relative Saturations*									
	ℓ/sec	GPM	$CaCO_3$	$CaSO_4 \cdot 2H_2O$	$Mg(OH)_2$	pH	% of recycle	ℓ/sec	GPM	moles/sec	ℓ/sec	GPM
Alternative 1	1,000	16,000	6.69	1.06	0.02	9.07	30	87	1,380	1.056	0	0
Alternative 2	950	15,000	5.06	1.07	0.02	9.01	36	103	1,624	1.366	0	0
Alternative 3	985	15,600	7.52	1.06	0.02	9.15	27	77	1,220	0.876	0	0
Alternative 4	1,035	16,400	29.13	0.98	0.16	9.76	0	0	0	0	51	810

*Critical values, avove which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$, about 2.5 for $CaCO_3$, and about 3.4 for $Mg(OH)_2$ (see Appendix C).

In the first three alternatives, softening was employed in the recycle stream to reduce the calcium content of the recycle. The rate of calcium removal required was determined by the relative saturation of $CaSO_4$ in the slurry line. In each case the relative saturation was near 1.0, well below the critical scaling level of 1.3-1.4. In the fourth case the rate of ash pond effluent was determined so that the relative saturation of $CaSO_4$ was slightly below 1.0.

The calcium was removed from a slipstream taken from the recycle line. The calcium concentration in the slipstream was assumed to reach 50 mg/ℓ. Actual equilibrium concentrations ranged from 22 to 29 mg/ℓ. The percent of the recycle flow that was treated was determined by the required calcium removal rate. Sample calculations are presented in greater detail in Appendix K.

In all four cases the relative saturation of $CaCO_3$ in the slurry was above the critical scaling value of 2.5. This value was actually smallest for the worse quality water because of the greater calcium removal rate required to control gypsum scale. $CaCO_3$ scale formation in the slurry line may possibly be reduced by installing a reaction tank prior to the sluice line. Sizing this tank is critical to the successful operation of this ash sluicing configuration. Additional data should be taken on a pilot scale so that the reaction tanks may be accurately sized before implementing this alternative. Pilot or bench scale testing to determine the level of acid washing that is sufficient to prevent the line from plugging should be conducted before these alternatives are implemented.

3.2.3 Effect of $CaSO_4 \cdot 2H_2O$ Supersaturation in the Pond Recycle Water

If the pond recycle water in a recirculating ash sluice system proposed for Montour remains supersaturated with respect to gypsum, scaling may occur in the fly ash sluice line. The degree of supersaturation in the pond recycle water cannot be accurately quantified but will depend on the degree of turbulence in the pond and on the residence time in the pond. The greater the degree of mixing in the pond due to thermal gradients or wind turbulence, the more desupersaturated the liquor will become. Longer residence times will also encourage gypsum precipitation.

However, the lack of $CaSO_4 \cdot 2H_2O$ crystals in the pond will discourage any precipitation and therefore, limit the degree of desupersaturation. Since ponds are generally not very well mixed, the pond will most likely remain supersaturated with respect to gypsum as long as no chemical treatment is used, and scaling may occur. Pilot or bench scale testing may provide information to more accurately determine the degree of desupersaturation.

In the simulations presented in Section 3.2.2, the pond water was allowed to remain supersaturated with respect to $CaSO_4$. This presented a worse case operation with respect to the amount of calcium that was required to be removed in order to inhibit $CaSO_4$ scale formation in the slurry line. Thus, if any precipitation does occur in the pond in actual operation, the softening load would be less than predicted from the simulations.

3.2.4 Effect of Carbon Dioxide Mass Transfer

Six additional cases were studied to determine the effects on the operation of the ash sluicing system of carbon dioxide mass transfer between the process liquor and the atmosphere. The results from these additional cases along with the three base cases previously discussed are shown in Table 3-7.

The three base cases used were similar to the first three alternatives presented in Table 3-6. In the base case simulations the pond was assumed to be in equilibrium with the atmosphere with respect to carbon dioxide but no transfer was allowed to occur in the slurry tank. For each base case two more simulations were performed where: (1) No CO_2 transfer in the tank or pond was allowed, and (2) CO_2 equilibrium with the atmosphere was attained in both the tank and the pond. For purposes of comparison softening was not employed in any of these simulations, as was done in the previous section.

From Table 3-7 it can be seen that the relative saturation of $CaSO_4$ in the slurry line is not strongly influenced by the degree of CO_2 transfer. In all three systems the relative saturation of $CaSO_4$ was slightly higher (less than 2%) for the simulations where no CO_2 transfer was allowed. For all the simulations the relative saturation of $CaSO_4$ remained near three.

TABLE 3-7. THE EFFECT OF CO_2 TRANSFER IN RECIRCULATING ASH SLUICING SYSTEMS AT MONTOUR

Makeup Water*	CO_2 Equilibrium in Sluice Tank	CO_2 Equilibrium in Pond	Fly Ash Slurry Relative Saturations** $CaCO_3$	$CaSO_4 \cdot 2H_2O$	$Mg(OH)_2$	pH	Pond pH
A	No	No	6.31	3.19	2.47	10.10	10.14
A	Yes	Yes	3.20	3.15	1.1×10^{-4}	7.90	7.71
A	No	Yes	17.77	3.15	0.02	8.98	7.71
B	No	No	4.84	3.83	2.72	10.04	10.06
B	Yes	Yes	3.02	3.78	1.3×10^{-4}	7.90	7.69
B	No	Yes	16.24	3.79	0.02	8.92	7.69
C	No	No	2.21	2.85	2.86	10.22	10.24
C	Yes	Yes	2.76	2.80	7.5×10^{-5}	7.88	7.73
C	No	Yes	17.65	2.80	0.02	9.06	7.73

*Makeup Water Sources:

A: 8 cycle cooling tower blowdown
B: 20 cycle cooling tower blowdown
C: River Water

**Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$, about 2.5 for $CaCO_3$, and about 3.4 for $Mg(OH)_2$ (see Appendix C).

The pH of the slurry effluent is strongly affected by the amount of CO_2 dissolved in the slurry water. In all three systems the highest pH's (over 10) occurred when no CO_2 transfer was allowed. The lowest pH's (under 8) occurred when CO_2 equilibrium was attained in both the pond and the slurry tank.

The relative saturations of $Mg(OH)_2$ and $CaCO_3$ are very pH dependent. As expected, the relative saturation of $Mg(OH)_2$ varied directly with the pH in the slurry. The lowest relative saturations of $Mg(OH)_2$ (near 10^{-4}) occurred when CO_2 equilibrium in both the tank and the pond brought the pH's below eight. The largest relative saturations (near 2.5) occurred when the lack of CO_2 transfer in both the tank and the pond allowed the pH to remain high.

The relative saturation of $CaCO_3$ is pH dependent because of the effect pH has on the carbonate-bicarbonate equilibrium. The variation in the relative saturation of $CaCO_3$ is due to the variation in the concentration of $CO_3^=$, which depends on both the pH and the total amount of carbonate species in the water. Because CO_2 was free to enter the system in some of the cases a simple relationship between pH and the relative saturation of $CaCO_3$ was not seen. In all three systems the largest relative saturation of $CaCO_3$ (above 16) occurred when equilibrium between the atmosphere and the pond was allowed and no CO_2 transfer took place in the slurry tank. This large relative saturation occurred because the pond served as a source of CO_3 and the pH in the tank did not reach as low a level as it did when CO_2 transfer occurred in the tank. Therefore, the reduction in pH caused by CO_2 transfer in the tank reduced the relative saturation of $CaCO_3$ more than the increase in total amount of carbonate species increased it for the cases where CO_2 equilibrium occurred in both the tank and the pond.

These results show that the best operating conditions, with respect to scale formation, would exist when CO_2 equilibrium was encouraged in both the tank and the pond. Although CO_2 transfer has not been quantified in this study, pilot scale studies to determine the optimum ash sluicing recycle configuration may provide data to allow a more accurate account of the level of CO_2 transfer in actual operations.

3.2.5 Arsenic Discharges

From the ash leaching studies discussed in Appendix D information about the amount of arsenic in the ash was obtained. Although Appendix D is concerned purely with calculations about the input species required for the computer simulations, using the same method, it was found that arsenic composed about 2.75×10^{-4} weight percent of the ash.

An estimate of the concentration of arsenic in the pond liquor for the four alternatives discussed was made by performing a mass balance around the ash sluicing system. It was assumed that all of the arsenic was leached from the ash and remained in solution. It was further assumed that all of the arsenic entered the system with the ash and left in the sludge water and pond discharge. In the first three alternatives the arsenic concentration rises to 1.3 mg/ℓ. In the fourth alternative the arsenic concentration is about 0.6 mg/ℓ because a discharge of 25 ℓ/sec (500 GPM) is taken from the pond for each unit. The calculations required for the fourth alternative are presented below.

$$\text{As (in discharge)} = \frac{\text{As (in with ash)}}{H_2O\text{ (discharged)} + H_2O\text{ (sludge)}}$$

$$= \frac{\left[(8621)^{\text{gm}} \left(\frac{.000275}{100}\right) 1000\right] \text{ mg/sec}}{(25.5 + 17.8)\ \ell\text{/sec}}$$

$$= 0.55 \text{ mg/}\ell$$

Actual arsenic concentrations may be lower than these values since equilibrium or rate relationships between the arsenic in the solid phase and arsenic in the liquid phase were not considered. In the closed-loop bench-scale recirculating studies, arsenic concentrations were found to be between 0.09 and 0.20 ppm, with an average value of 0.14 ppm. These values are significantly less than the calculated values of 1.3 and 0.6 ppm.

3.2.6 Conclusions

From the results presented above the following conclusions can be made about the ash sluicing system at Montour.

1) Any recirculating ash sluicing system at Montour will require either softening or a blowdown to control $CaSO_4$ scale in the slurry line.

2) The amount of softening required is dependent on the degree to which $CaSO_4$ precipitates in the pond.

3) The degree of CO_2 transfer in the tank and the pond strongly affects the relative saturation of $CaCO_3$ and $Mg(OH)_2$ but does not significantly affect the $CaSO_4$ scale potential.

3.3 Summary

From the results of the cooling tower and ash sluice system simulations discussed in the previous sections, four alternatives for reducing plant discharges are considered technically feasible. These are:

1) Cooling tower operation at 8 cycles with 24 ℓ/sec (380 GPM) blowdown and the design drift rate of 31 ℓ/sec (500 GPM) and recirculating ash sluicing using cooling tower blowdown as makeup. This alternative requires acid treatment in the towers and slipstream softening for calcium removal from the ash pond recycle. (Zero discharge)

2) Cooling tower operation at 20 cycles with 20 ℓ/sec (325 GPM) blowdown and no drift, and recirculating ash sluicing, using cooling tower blowdown as makeup. This alternative also requires acid addition in the towers and softening in the ash system. (Zero discharge)

3) Cooling tower operation at 20 cycles with no blowdown and a drift rate of 20 ℓ/sec (325 GPM) and recirculating ash sluicing, using river water as makeup. Again, acid addition in the towers and softening in the ash system are required. (Zero discharge)

4) Cooling tower operation at 20 cycles with no blowdown and a drift rate of 20 ℓ/sec (325 GPM) and recirculating ash sluicing using river water as makeup. This alternative only requires acid treatment in the towers. [Discharge - 51 ℓ/sec (810 GPM)]

All of these alternatives will require the addition of sulfuric acid in the cooling towers for $CaCO_3$ scale control and reaction tanks prior to the fly ash sluice line to minimize $CaCO_3$ and $Mg(OH)_2$ scale formation in the line. Adjustment of the pH of the ash pond overflow may be required in Alternative 4, depending on the amount of carbon dioxide mass transfer occurring in the pond. (Section 3.2.4) The first three alternatives employ soda-ash softening of a portion of the ash pond recycle. This treatment is necessary to prevent $CaSO_4$ scale potential in the sluice line. The fourth alternative controls the gypsum scale potential without softening by employing a small blowdown of 51 ℓ/sec (810 GPM) from the pond.

The first two alternatives differ only in the assumption concerning the drift rate in the cooling towers. The operating conditions are essentially the same. Therefore, these two are not really different alternatives but represent the extremes in water quality that might be seen from a cooling tower operating with a blowdown of about 22 ℓ/sec (350 GPM). The quality of this blowdown stream has significant effects on the ash sluicing system since it serves as makeup to the system.

Alternatives 3 and 4 assume that the drift rate would not fall below 65% of the design value. Even with this small drift rate the cooling towers could be operated at zero discharge using sulfuric acid to prevent $CaCO_3$ scale. The ash sluicing makeup water can be supplied directly from the river or pond since there will be no cooling tower blowdown. This higher quality water allows for less treatment of the ash recycle than would be needed in Alternatives 1 and 2. Alternative 4 represents the smallest discharge that could be expected if softening were not used.

It should be emphasized here that none of the alternatives should be implemented before more information is gathered from a bench or pilot scale test program to determine 1) the actual size of reaction tank required in the sluice system, 2) the quantity and frequency of acid wash water required to minimize $CaCO_3$ and $Mg(OH)_2$ scale formation, and 3) the true drift rate in the cooling towers.

An economic analysis based on rough cost estimates for these alternatives is presented in the next section.

4.0 ECONOMICS

This section provides rough cost estimations for implementing each of the technically feasible alternatives discussed in Section 3.0. Both rough capital costs and operating costs are presented. The assumptions used in calculating these costs are briefly outlined. It is emphasized that these values are only rough estimates for comparative purposes.

The capital cost summary for the four technically feasible alternatives is presented in Table 4-1. All the alternatives involve sluicing the fly and bottom ash at about 5 wt. % solids and require identical tanks and agitators. Since the flows do not differ significantly among alternatives the pumping and piping capital costs are the same. The capital expenditures for softening vary directly with the size of the treated stream.

The costs reported for the fly ash slurry tanks include two 39,000 gallon, carbon steel, neoprene-lined tanks, with mixer support structures and baffles. These tanks were sized to give a fifteen-minute residence time for 2580 GPM of fly ash slurry from each unit. The costs are for nominal foundations and plumbing. The terrain and soil characteristics may require special site preparation which will add to tank installation costs, and the costs for interconnecting plumbing and piping will also be a function of the particular site. Field erection rates are based on national average rates but can vary widely with the specific location and labor pool used.

The costs for the agitators are based on two 10 hp, electrically-driven, neoprene-coated agitators. The costs for both the tanks and the agitators were obtained from (GU-075) in 1970 dollars and upgraded to 1976 using a factor of 1.56 (based on Chemical Engineering Index).

The first three alternatives require approximately 10,000 GPM of the pond water to be recycled to both units. The fourth alternative requires about 9,000 GPM of the pond water for recycle. The costs reported for piping include the cost of 1,400 feet of 24-inch carbon steel pipe with average fittings, flanges, shop coating, and wrapping. The values were estimated from (GU-075) in 1970 dollars and upgraded to 1976 using a factor of 1.56.

TABLE 4-1. CAPITAL COSTS[1] FOR WATER RECYCLE/REUSE ALTERNATIVES AT MONTOUR

	Alternative 1	Alternative 2	Alternative 3	Alternative 4
Fly Ash Slurry Tanks[2]	100,000	100,000	100,000	100,000
Agitators	14,700	14,700	14,700	14,700
Pond Overflow Recycle Pumps	93,400	93,400	93,400	93,400
Pond Overflow Recycle Piping	144,000	144,000	144,000	144,000
Additional Fly Ash Slurry Pumps	42,000	42,000	42,000	42,000
Sodium Carbonate[3] Softening	126,500	148,900	111,900	0
Contingency (20%)	104,000	108,600	101,200	78,800
Contractual Fees (3%)	15,600	16,300	15,200	11,800
TOTAL	640,200	667,900	622,400	484,700

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[1] 1976 dollars (rough cost estimates for comparative purposes)

[2] includes wear liner and agitator supports

[3] $91.7/GPM

Pump costs were estimated based on cast steel pumps with electric motor drivers. A labor-to-material ratio of 0.36 was used for installation costs. Engineering was assumed to be 10% of the combined labor and material cost (GU-075).

The softening costs were estimated from (NE-107). A cost of $91.7/GPM of installed capacity was used. The cost for the four alternatives vary because of the variation in the slipstream rate required for softening.

The operating cost summary for the four technically feasible alternatives is presented in Table 4-2. The operating cost vary directly with the capital costs. Thus, the alternative requiring the most amount of capital also requires the largest operational budget.

The power consumption is the same for all but the fourth alternative. This is because the recycle is about 9,000 GPM in Alternative 4 as opposed to about 10,000 GPM in the others. The costs are based on a wholesale price of 2¢/kW-hr to the utility.

The cooling tower treatment costs vary directly with the cycles of concentration of the recirculating flow in the towers. In Alternative 1, the cooling towers are operated at 8 cycles of concentration compared to the other alternatives where the cycles of concentration is increased to 20. The treatment costs only include the cost of sulfuric acid at $60/ton.

The softening costs are the dominant operating cost other than capital charges. Alternative 4 costs significantly less than the others because softening is not employed and capital charges are smaller. The softening costs include only the cost of chemicals at $69 per million gallons treated. The capital charges were estimated as 15% (MC-136) of the capital investment shown in Table 4-1 for each alternative based on a 30-year lifetime.

The costs presented in this section are merely rough estimates. They are presented here in order to compare the relative cost of each alternative. They do not include any savings that might occur because of reduced makeup water requirements.

TABLE 4-2. OPERATING COSTS[1]

	Alternative 1	Alternative 2	Alternative 3	Alternative 4
Cooling Tower[2]				
Acid Treatment	2,800	5,600	5,600	5,600
Power Consumption[3]				
Agitators				
Recycle Pumps	34,200	34,200	34,200	24,600
Softening Chemicals[4]	40,000	47,100	35,400	0
Capital Charges[5]	96,000	100,200	93,400	72,700
TOTAL	173,000	187,100	168,600	162,900
(mils/kW-hr)	(.016)	(.018)	(.016)	(.010)

[1] 1976 dollars per year based on 80% load factor

[2] \$60/ton for sulfuric acid

[3] 2¢/kW-hr

[4] \$69/10^6 gal (chemicals cost only)

[5] 15% per year based on 30-year lifetime

Appendix J. Recycle/Reuse Options at Colstrip (Montana Power Company)

1.0 INTRODUCTION

This appendix describes the analysis of the water system at Montana Power Co.'s (MPC) Colstrip plant, under EPA Contract No. 68-03-2339, Water Recycle/Reuse Alternatives in Coal-Fired Power Plants. A summary of the important results is presented in this section. Colstrip was chosen along with four other plants for evaluation of technical and economic feasibility of various water recycle/reuse options.

Three major topics are discussed in this appendix:

1) Existing Operations Modeling
2) Alternatives Modeling
3) Economics

The major water systems at the two-unit, 700 Mw Colstrip plant are the cooling tower and combined SO_2/particulate scrubbing systems. Colstrip is designed for and is achieving zero discharge through brine concentration of the cooling tower blowdown and a disposal pond for the scrubber sludge.

The results of the existing operations simulations of the cooling towers compare well to the sample data obtained at the plant with respect to $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ scale potential. The simulations performed indicate that the towers are presently operating at about the maximum cycles of concentration obtainable without approaching gypsum scale potential.

The results of the existing operations simulation of the scrubbing system compare well to the sample results for the scrubber recycle stream with respect to magnesium, sodium, and chloride. Calcium and sulfate concentrations were lower in the sampled stream, most probably due to reduced load and/or reduced SO_2 content in the gas from design conditions, resulting in a lower mass removal rate of sulfur from the gas.

Process alternatives at Colstrip were studied on a modular basis with the cooling system being one module and the scrubbing system being the other. A total of six cooling tower simulations were performed to compare treatment alternatives and determine the effects of calcium and sulfate concentrations in the makeup water on slipstream treatment rate. The first set of simulations comparing treatment alternatives shows that with the use of slipstream softening, as opposed to the present pretreatment system, cycles of concentration may be increased from 13.5 to 20. The towers may only be operated at a maximum of about 11 cycles of concentration without any softening based on the makeup water sampled.

The additional simulations showed that calcium had a greater effect on slipstream treatment rate than sulfate in the makeup water. Doubling the calcium concentration increased the treatment rate about 370% whereas doubling the sulfate concentration only increased the treatment rate about 37%.

No scale potential was found for any phosphate or silica solids even at 20 cycles of concentration, which is the highest value considered.

A total of four additional scrubbing simulations were performed to examine the effects of flue gas ash content, slurry percent solids, and makeup water source on the scrubber operation at Colstrip. As the ash rate into the scrubbers increases, and as the percent solids in the circulating liquor decreases, $CaSO_4 \cdot 2H_2O$ scale potential is increased. Therefore, burning a coal of significantly higher ash content or operating the system at low solids in the recycle loop could cause scaling problems because of the small percentage of calcium sulfate seed crystals present in the slurry.

The use of either untreated river water or cooling tower blowdown as makeup (excluding demister wash) to the scrubbing system does not have a significant impact on the scaling tendency of the system. The use of cooling tower blowdown increases the total dissolved solids and chloride levels, but these levels should not be high enough to cause corrosion problems.

Table 1-1 presents a summary of the two combined system alternatives for the Colstrip water system as compared to existing operations and the relative costs of each alternative. All flows reported in Table 1-1 refer to those produced from both units. It should be noted here that this analysis was performed to study general water recycle/reuse alternatives. Actual implementation of any of these alternatives would require a more extensive investigation of process parameter variability. More data on makeup water quality, scrubber variations and seasonal flow variations would be required before a detailed design could be made.

TABLE 1-1. SUMMARY OF WATER RECYCLE/REUSE OPTIONS AT COLSTRIP

	Existing Conditions	Alternative One	Alternative Two
Cooling Tower Makeup Source	Softened River Water	Softened River Water	Untreated River Water
Cycles of Concentration in Cooling Towers	13.5	13.5	20
Cooling System Treatment	Makeup Softening	Makeup Softening	Slip-stream softening
Treatment Rate, ℓ/sec (GPM)	423 (6710)	397 (6300)	18 (284)
Cooling Tower Blowdown Rate, ℓ/sec (GPM)	23.6 (376)	23.6 (376)	14.6 (230)
Scrubber Makeup Source	Softened River Water, Brine Concentrator Distillate	Cooling Tower Blowdown, Untreated River Water	Cooling Tower Blowdown, Untreated River Water
Plant Makeup Rate ℓ/sec (GPM)	423 (6710)	423 (6710)	423 (6710)
Plant Discharge Rate ℓ/sec (GPM)	0.	0.	0.
Costs:[1]			
Capital, 1976 $	--	159,000	275,000
Operating, 1976 $/yr.[2]	--	-237,000	-217,000
(mils/kwh)	--	(-.046)	(-.044)

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[1] These rough cost estimates were made to compare technically feasible options and do not include a "difficulty to retrofit" factor.

[2] Includes capital cost amortization at 15% per year.

The first alternative does not involve any changes in operation of the cooling towers but uses cooling tower blowdown and untreated river water as scrubber makeup as opposed to softened river water and brine concentrator distillate as is presently done. A capital cost of $159,000 is reported for piping modifications and new pumps. However, a net operating savings is shown due to a large savings in brine concentrator operation because of the reduced flow. Only enough cooling tower blowdown is sent to the brine concentrator to provide the boiler makeup requirements (only one brine concentrator needed).

Alternative 2 includes using slipstream treatment in the cooling tower system in addition to the system changes of Alternative 1. The towers are operated at 20 cycles of concentration resulting in decreased blowdown. Again only enough cooling tower blowdown to provide the boiler makeup is sent to the brine concentrator. A higher capital cost is reported due to the conversion to slipstream treatment in the cooling system. The increased capital charges result in a lower operating expense savings for this alternative. The savings in brine concentrator operating costs represents the major savings of both of these alternatives.

Although the Colstrip plant is achieving zero discharge, more effective cascading of the water streams in the plant may be achieved which results in a decrease in operating costs from the existing level. The capital and operating costs reported in this appendix do not include any savings which could have been realized if the Colstrip water system had been designed for the most effective cascading of aqueous streams. A savings in capital investment could have been achieved by designing the cooling towers for slipstream treatment (was not considered reliable enough at the time of Colstrip design) and by using only one 150 GPM capacity brine concentrator as opposed to the two 200 GPM capacity units presently used. The capital savings associated with purchasing one 150 GPM brine concentrator versus two 200 GPM units totals about $1.9 million based on $7,750/GPM (LE-239).

2.0 PLANT CHARACTERISTICS

The Montana Power Co. (MPC) Colstrip Plant is located in Colstrip, Montana, and consists of two 350 Mw coal-fired units. The coal burned at Colstrip is taken from a mine located adjacent to the plant and contains from .2 to 1% sulfur and 6.1 to 12.6% ash (average values reported by MPC are .77% and 8.59%, respectively). The heating value of the coal is approximately 8500 Btu/lb as received. Colstrip is designed to achieve zero discharge with cooling towers, a recirculating bottom ash sluice system, and combined particulate and SO_2 scrubbing with disposal ponds.

This section of the appendix describes the characterization of Colstrip's water system. First, an overall plant water balance is presented which shows the major in-plant flows and chemical analyses for the streams which were sampled. Then a detailed discussion of each of the major water consumers is presented, including a description of the process model and the input data used to simulate design conditions at Colstrip. The computer simulation results are compared to the chemical analyses of the spot samples. Areas of Colstrip's water system which show a potential for increased water recycle/reuse are also identified and discussed.

2.1 Water Balance

A flow schematic for the Colstrip water system is shown in Figure 2-1. The major water consumers which include the cooling tower and scrubbing systems are shown in this diagram. This figure presents design flows and results of the chemical analyses of the samples taken at Colstrip. A more detailed description of the samples taken and analytical procedures used is presented in Appendix B. As shown in Figure 2-1, makeup water for the plant is taken from the Yellowstone River and stored in a surge pond. The water taken from the pond is treated with cold lime softening for calcium removal. The lime-treated water is then used as makeup water to the cooling tower and scrubbing systems. Softening wastes are sent to the scrubber ponds.

Cooling tower blowdown is piped to two 12.6 ℓ/sec (200 GPM) capacity brine concentrators. The distillate provides the demineralizer feed (design rate of about 90 GPM, actual rate of 100-200 GPM). Excess distillate is combined with lime-softened water and used as scrubber makeup. The concentrated waste from the brine concentrators is disposed of in two one-acre lined ponds.

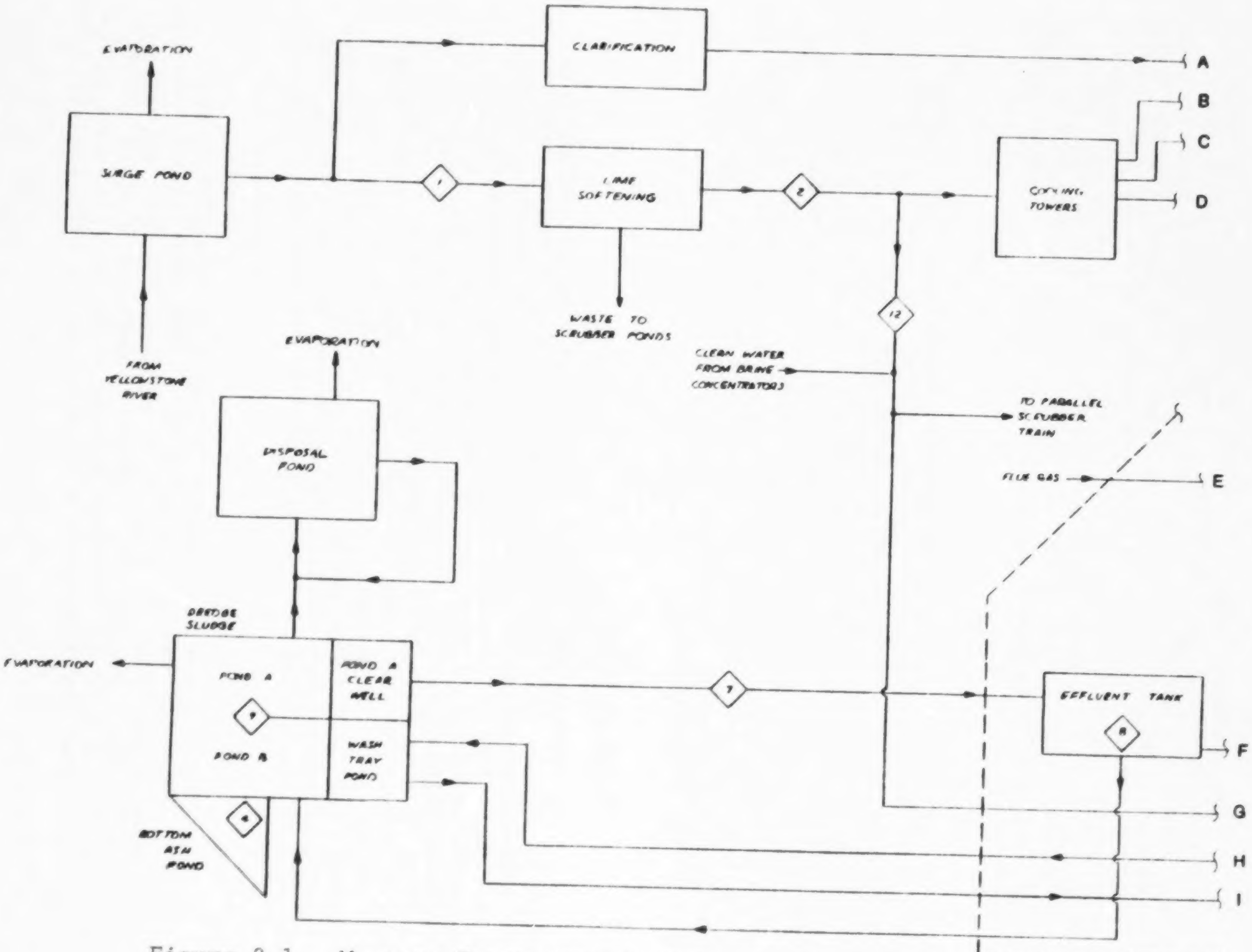


Figure 2-1. Montana Power Company Colstrip Plant water balance.

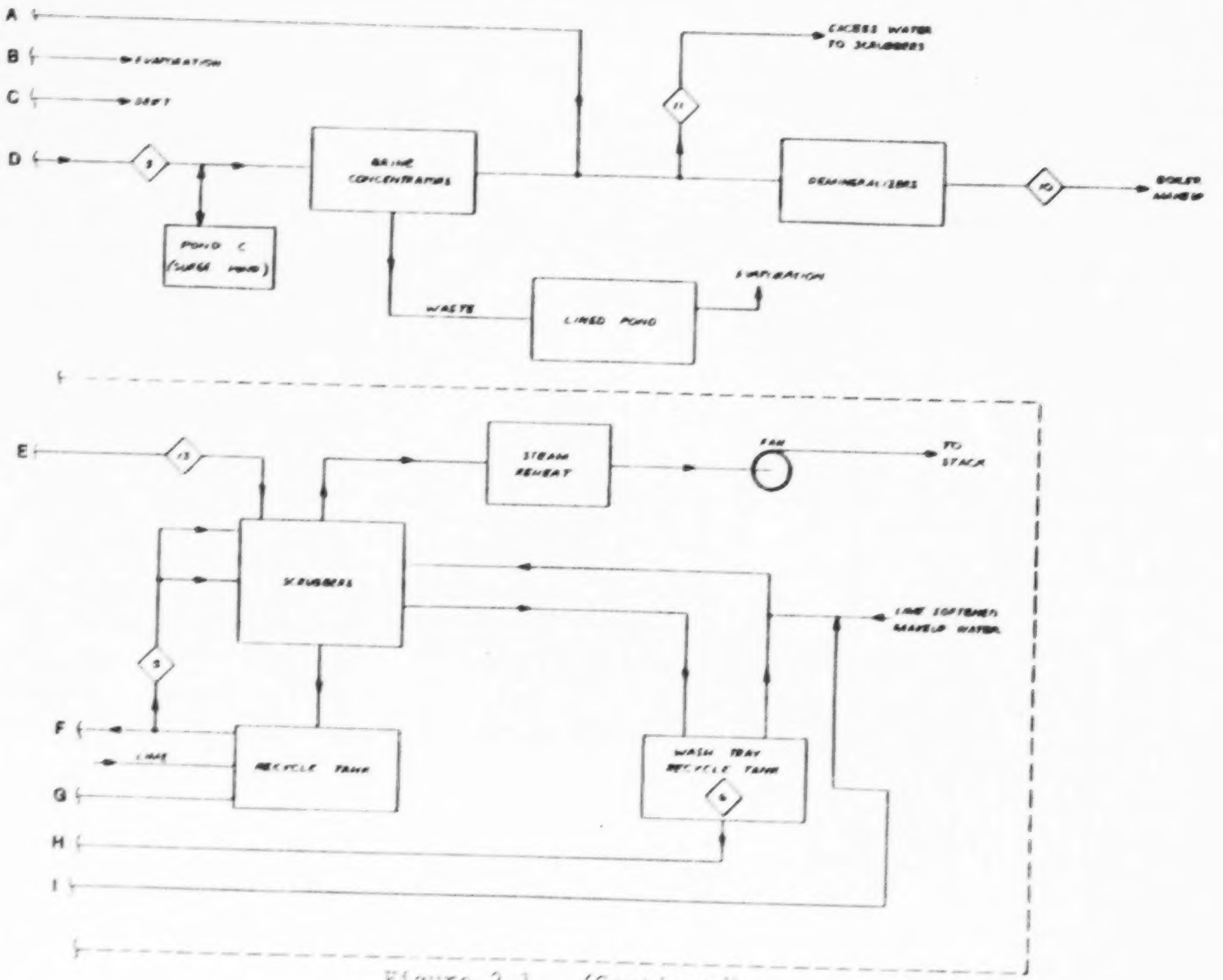


Figure 2-1. (Continued)

Stream Number	1	2	3	4	5	6	7	8	9	10	11	12	13
Stream Name	Plant Makeup Water	Softened Makeup Water	Cooling Tower Blowdown	Bottom Ash Sluice Water	Scrubber Recycle Slurry*	Wash Tray Recycle Tank Liquor	Pond Recycle	Effluent Tank Slurry*	Pond Liquor	Boiler Makeup	Brine Concentrator Water To Scrubbers	Lime Treated Water To Scrubbers	Flue Gas*
Flow: **Metric English	423 l/sec. 6,710 gpm	423 l/sec. 6,710 gpm	25.2 l/sec. 400 gpm	38.2 l/sec. 605 gpm	961 l/sec. 15,240 gpm		105 l/sec. 1,665 gpm	19.9 l/sec. 315 gpm		5.6 l/sec. 88 gpm	19.7 l/sec. 312 gpm	25.5 l/sec. 404 gpm	810,000 m^3/hr 477,000 acfm
pH	6.7	10.3	6.7	10.4	5.5	3.4	5.3	4.4	4.8			10.3	
Calcium	57.9	39.9	533	711	506	519	484	497	464			39.9	
Magnesium	10.5	10.7	185	76	5,006	2,925	1,306	2,075	1,600			10.7	
Sodium	53.5	53.1	710	295	458	153	305	315	345			53.1	
Potassium	4.2	4.2	50.3	23.1	21.9	11.5	12.1	15.5	23.1			4.2	
Chloride	22	17	164	79	229	67	75	76	76			17	
Carbonate (as CO_3)	17.3	6.0	34.8	7.2	57.3	25.2	9.6	21.2	9.5			6.0	
Sulfate (as SO_4)	174	188	1,825	2,780	19,400	15,600	9,006	11,800	9,511			188	
Sulfite (as SO_3)					205	1,360	406	156					
Nitrate (as NO_3)	1.7	1.4	11.2	68	141	86.6	130	118	136			1.4	
Phosphate (as PO_4)			0.26				0.01	0.008					
Silicates (as SiO_2)	1.8	1.3	5.0	1.4	31	22	24	25	21.4			1.3	
Suspended Solids	0.002	0.0016	0.0014	0.0048	1.7	0.08	0.0016	1.36	0.01			0.0016	
Dissolved Solids	440	360	6,300	4,300	29,200	16,200	13,600	17,200	14,400			360	

*Flows reported are for each scrubber module.

**Flows are reported as design flow under full load operation for both units except where noted.

Figure 2-1. (Continued)

The portion of Figure 2-1 encircled by the dotted line represents one scrubber train. There are three identical trains on each of the two generating units. The scrubbing system makeup water is added along with lime to the recycle tank in each train. The dust-laden, SO_2-rich flue gas enters the scrubber venturi section at the top of each train and flows down cocurrently with the scrubber recycle liquor. The gas then is channeled through a 180° bend and flows upward through the spray section for SO_2 removal. The scrubbing liquor which is sprayed countercurrently to the gas stream falls into the recycle tank and the clean gas passes through a mist eliminator section and exits at the top of the scrubber. The exit gas then passes through a steam reheat section and an induced draft fan before being vented through the stack.

Mist eliminators are washed by a separate recirculating stream. The wash water is collected by a wash tray and recycled through a wash tray recycle tank. There is one wash tray recycle tank for every three modules. A portion of the wash water is pumped to the wash tray pond for solids settling. Clear liquor is returned to the spray headers. Lime-softened makeup water and brine concentrator distillate are added to replace water lost through evaporation and occlusion with the solids.

A bleed stream is taken from the scrubber recycle tank, diluted to about 6% solids with pond recycle liquor in the effluent tank, and pumped to the pond system. At the present time, scrubber solids are dredged from Pond A and slurried to a disposal pond. Excess pond liquor is recycled to the scrubbers. There is one effluent tank for every three modules.

Bottom ash at Colstrip is sluiced to the bottom ash pond in a recirculating system. Clear liquor from the bottom ash pond clear well is used as sluice water. Makeup to this system results from plant drainage water which flows into the bottom ash pond. A blowdown from the bottom ash sluicing system results from bottom ash pond overflow into Pond B.

There are no aqueous discharges from the Colstrip Plant. Water losses occur through cooling tower evaporation and drift, scrubber evaporation, pond evaporation, solids occlusion, and boiler losses.

The first step in characterizing the chemistry of the Colstrip water system is to examine the results of the spot samples taken. The measured species concentrations were input to the equilibrium program and several parameters were calculated which determine the tendency of the liquor sampled to form chemical scale and to absorb or desorb CO_2 from the atmosphere. Another parameter calculated checks the internal consistency of the sample and is a measure of the analytical accuracy.

Table 2-1 presents a summary of the parameters calculated by the equilibrium program for each of the samples taken at Colstrip. Relative saturations for $CaCO_3$, $Mg(OH)_2$, and $CaSO_4 \cdot 2H_2O$ are given in the first three columns. These parameters indicate the tendency of the stream to form scale. Critical values for relative saturation of each species, above which scale formation is likely, are 2.5 for $CaCO_3$, 3.4 for $Mg(OH)_2$, and 1.3-1.4 for $CaSO_4 \cdot 2H_2O$. (See Appendix C)

Only one stream, the bottom ash sluice water, showed a tendency to form $CaCO_3$ scale (relative saturation of 4.55). The erosive character of an ash slurry stream may prevent excessive buildup of the $CaCO_3$ scale, since no plugging problems have been encountered. The bottom ash sluice water also showed a relative saturation for $CaSO_4 \cdot 2H_2O$ above the critical range of 1.3-1.4. Gypsum formation has been noted in the bottom of the boiler where the bottom ash sluice water contacts the hot ash.

The pond recycle, effluent tank, and pond liquor samples all showed $CaSO_4 \cdot 2H_2O$ relative saturations in the critical range. Although no scaling has been reported, operation of the scrubbers in this range may result in some gypsum scale formation over a long period of time. None of the streams sampled showed a tendency to form $Mg(OH)_2$ scale (the highest relative saturation calculated was .264 in the bottom ash sluice water).

Equilibrium partial pressures of CO_2 above the liquor sampled were calculated by the equilibrium program and show the tendency of a stream to absorb or desorb CO_2 when in contact with the atmosphere. A value less than 3×10^{-4} atm. indicates a tendency to absorb CO_2 and a value greater indicates a tendency to desorb CO_2. The value for the cooling tower blowdown sample is higher than 3×10^{-4} indicating that complete CO_2 equilibrium is not achieved in the cooling towers.

Percent residual electroneutrality is a parameter calculated to determine the internal consistency of each sample with pH specified. A value of $\underline{+}15\%$ is considered acceptable. A more detailed explanation of how this parameter is calculated along with a description of the equilibrium program is presented in Appendix E (p. E-41).

TABLE 2-1. PARAMETERS CALCULATED BY EQUILIBRIUM PROGRAM FOR COLSTRIP SAMPLES

Stream Name	Relative Saturations*			Equilibrium partial pressure of CO_2, atm	% Residual Electroneutrality
	$CaCO_3$	$Mg(OH)_2$	$CaSO_4 \cdot 2H_2O$		
Surge Pond	.0026	7.8×10^{-9}	.041	1.91×10^{-3}	+23.8
Softened Makeup Water	1.08	.027	.034	1.00×10^{-7}	+ 7.3
Cooling Tower Blowdown	.051	5.9×10^{-7}	1.11	4.28×10^{-3}	-10.5
Bottom Ash Sluice Water	4.55	.264	1.67	2.59×10^{-8}	- 7.9
Scrubber Recycle Slurry	1.87×10^{-5}	7.2×10^{-10}	1.00	.511	+11.0
Wash Tray Recycle Slurry	1.2×10^{-6}	5.2×10^{-11}	.82	.240	+21.2
Pond Recycle	2.2×10^{-5}	2.7×10^{-10}	1.38	2.40×10^{-3}	-10.6
Effluent Tank Slurry	1.5×10^{-6}	2.0×10^{-11}	1.31	.0127	-13.9
Pond Liquor	1.5×10^{-6}	3.1×10^{-11}	1.30	2.96×10^{-3}	-13.7

*Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$, about 2.5 for $CaCO_3$, and about 3.4 for $Mg(OH)_2$ (see Appendix C)

2.2 Cooling Tower System

Each of the two 350 Mw units at Colstrip has an independent cooling system with one cooling tower per unit. Each tower has seven fans with a combined capacity of about 1.7×10^7 m^3/hr (1×10^7 ACFM). Water circulates at a design rate of 6510 ℓ/sec (103,200 GPM) between the condenser and cooling tower for each unit. A blowdown stream is removed from the circulating water after the condenser. Makeup water is added to replace the water lost in the blowdown and through evaporation and drift in the tower.

Presently, blowdown is removed from the cooling system at a rate which sets the cycles of concentration between 10 and 15, depending on the makeup water quality. Cycles of concentration may be defined as the ratio of blowdown species concentrations to makeup species concentrations. In terms of flow rates, cycles of concentration is:

$$C = \frac{E + B + D}{B + D}$$

where C = cycles of concentration

E = evaporation rate

B = blowdown rate

D = drift rate

This equation shows that as the blowdown decreases, the cycles of concentration increases, assuming that evaporation and drift remain constant.

The following sections present the model used to simulate the Colstrip cooling tower system and the results of existing operations simulations. A more detailed description of the tower operating parameters is also presented in the following sections.

2.2.1 Simulation Basis

Existing operations simulations were performed for the Colstrip cooling tower system to verify the validity of the simulation model in predicting scaling tendencies in the tower and to determine any potential for increased recycle/reuse.

This section first briefly discusses the model followed by a description of the operating parameters used as inputs to the model. A detailed description of the process model is included in Appendix E.

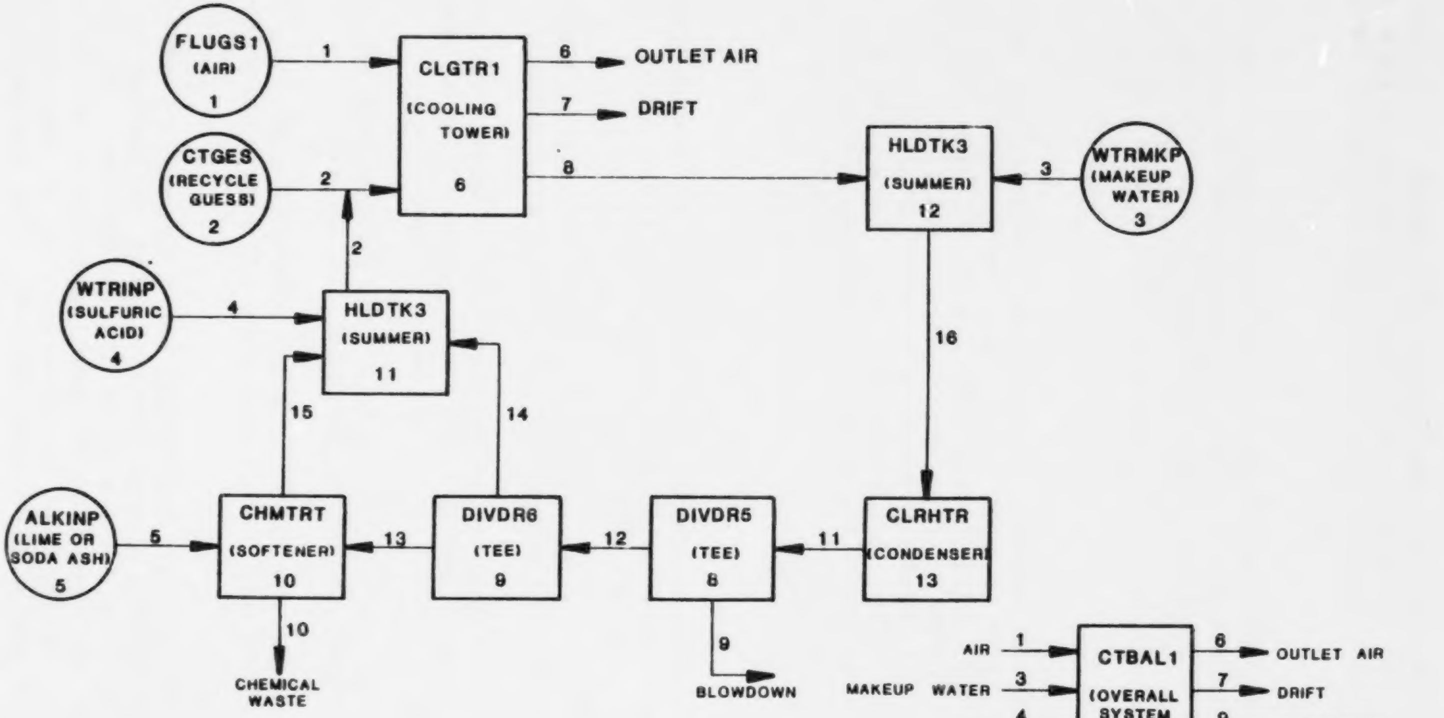
The process simulation flow scheme shown in Figure 2-2 was used to model cooling tower operations at Colstrip. This is a generalized cooling tower model with capabilities of simulating sulfuric acid addition and slipstream softening for calcium removal. Only acid addition was used for existing operations.

Given the inputs of air flow, temperature and composition, makeup water composition, flow and temperatures of the circulating water, drift rate, and cycles of concentration, the model performs iterative calculations around the cooling loop to determine the blowdown, evaporation and makeup rates and compositions for all water streams. An acid addition rate is determined to keep the $CaCO_3$ relative saturation within a specified range. If slipstream softening is required (determined by model) the slipstream and chemical addition rates are calculated.

Several assumptions are inherent in performing this simulation with the subroutines shown in Figure 2-2. These assumptions are given below:

1) Equilibrium exists between CO_2 and H_2O in the atmosphere and cooling tower exit water.
2) The temperature of the cooled water stream approaches the wet bulb temperature of ambient air within a predictable range.
3) The compositions and temperatures of the cooled water and drift streams are equal.
4) Ionic reactions taking place in the liquid phase are rapid and thus at equilibrium.

The assumption involving the temperature of the cooled water stream is a recognized design parameter in cooling tower evaluation and gives a good approximation. The assumption concerning the temperature and composition of the drift stream should be very close to actuality as is the assumption in regard to H_2O gas-liquid equilibrium. The assumption with



ORDER OF PROCESS CALCULATIONS:
1, 2, 3, 4, 5, 6, 7, (12, 13, 8, 9, 10, 9, 11, 6, 7), 8 *

Figure 2-2. Colstrip cooling tower simulation flow scheme.

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regard to CO_2 equilibrium is conservative since the partial pressure of CO_2 in actual cooling towers tends to be greater than the equilibrium value. The lower equilibrium concentration of carbonate species, assumed in the model, causes the pH to be slightly higher in the model than in actual operation. The higher pH causes the relative saturation of $CaCO_3$ to increase more than the lowered carbonate species concentration causes it to decrease.

The data used as input to this model is presented in Table 2-2. Some of this information was obtained directly from MPC. Other inputs were calculated from MPC data, local meteorological data, and sample analyses. Air, drift, and circulating water flow rates were obtained from MPC as were the approach, condenser ΔT, and condenser outlet temperatures. Ambient air wet and dry bulb temperatures were obtained from local climatological data for Billings, Montana, for 1976. The water makeup composition was obtained from the spot sample taken at the Colstrip plant.

2.2.2 Simulation Results

This section describes the results from the simulation of existing cooling tower operations at Colstrip. One simulation was performed for summer operation and one for winter operation. Table 2-3 presents the results of these two simulations, along with the plant data concerning actual operation at the time the spot samples were taken.

The blowdown flow for summer operation compares well to the value reported by MPC for summertime operation (12.7 vs. 11.8 ℓ/sec). The blowdown pH's for the simulations are slightly higher than the sample value. This is most probably due to higher sulfate in the sample through excess acid addition at the plant. Also, higher sodium and magnesium values in the sample will allow increased complexing between sulfate and these cations. The higher cation solution can therefore tolerate higher sulfate levels while maintaining a relatively constant gypsum relative saturation. (Simulation value of 1.01 versus sample value of 1.11.)

Comparison of the blowdown compositions shown in Table 2-3 indicates that the system may not have been at steady state during sampling. For example, although the calcium concentrations agree very well for all cases, the magnesium and carbonate concentrations are higher in the sample and nitrate

TABLE 2-2. INPUT DATA FOR COLSTRIP COOLING TOWER SIMULATIONS

	Winter	Summer
FLOWS		
Air, m^3/hr (ACFM)	1.7x10^7 (1.0x10^7)	1.7x10^7 (1.0x10^7)
Drift, ℓ/sec (GPM)	1.3 (20)	1.3 (20)
Circulating water, ℓ/sec (GPM)	6,510 (103,200)	6,510 (103,200)
TEMPERATURES		
Ambient Air, °C (°F)	-1.1 (30)	20.6 (69)
Approach, °C (°F)	11.9 (21.5)	11.9 (21.5)
Condenser ΔT, °C (°F)	17.6 (31.7)	17.6 (31.7)
Wet Bulb, °C (°F)	-4.4 (24)	12.8 (55)
Condenser Outlet, °C (°F)	25 (77)	42.2 (108)
ADDITIONAL DATA		
Relative Humidity, %	42	40
Cycles of Concentration	13.5	13.5
Makeup Water Composition mg/ℓ		
Calcium	39.9	39.9
Magnesium	10.7	10.7
Sodium	40.3	40.3
Chloride	17.0	17.0
Carbonate (as $CO_3^{=}$)	6.0	6.0
Sulfate (as $SO_4^{=}$)	188.0	188.0
Nitrate (as NO_3^{-})	1.4	1.4

TABLE 2-3. COLSTRIP EXISTING COOLING TOWER OPERATIONS SIMULATION RESULTS

		Simulations (13.5 cycles of concentration)	
Cooling tower blowdown	Plant data	Case 1 Winter Operation	Case 2 Summer Operation
Flow, gpm per tower	202.*	138.	187.
(ℓ/sec)	(12.7)	(8.7)	(11.8)
pH	6.7	7.2	7.2
Composition, mg/ℓ			
Calcium	533	535.8	533.7
Magnesium	193	143.7	143.1
Sodium	710	541.6	539.5
Chloride	266	228.3	227.4
Sulfate (as $SO_4^=$)	3820	2652.	2644.
Carbonate (as $CO_3^=$)	34.8	10.1	6.5
Nitrate (as NO_3^-)	11.2	18.8	18.7
Relative Saturations**			
$CaCO_3$	.051	.06	.097
$CaSO_4 \cdot 2H_2O$	1.11	1.01	.93
Partial Pressure CO_2, atm	4.3×10^{-3}	4.5×10^{-4}	3.8×10^{-4}

* Based on 13.5 cycles and makeup rate from MPC.

** Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C) is lower in the sample. These discrepancies may also be due to nonhomogeneous sampling and/or analytical errors as well as non-steady-state operation.

The $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ relative saturations agree well between the sample and simulations. The values for $CaCO_3$ (.05-.097) indicate that the towers are operating in a very safe mode since the critical value for scale formation is about 2.5. This, along with the higher sample sulfate concentration and lower sample pH, supports the possibility of excess acid addition in the towers. Normal pH in the cooling system ranges from 7.8-8.0. The relative saturations for $CaSO_4 \cdot 2H_2O$ (.93-1.11) indicate that the towers are presently running at about the maximum cycles of concentration with respect to gypsum scale since the critical range for scale formation is 1.3-1.4. However, increased cycles may be obtainable if slipstream treatment is used instead of pretreatment. This allows more effective softening since the circulating water is more concentrated than the makeup water.

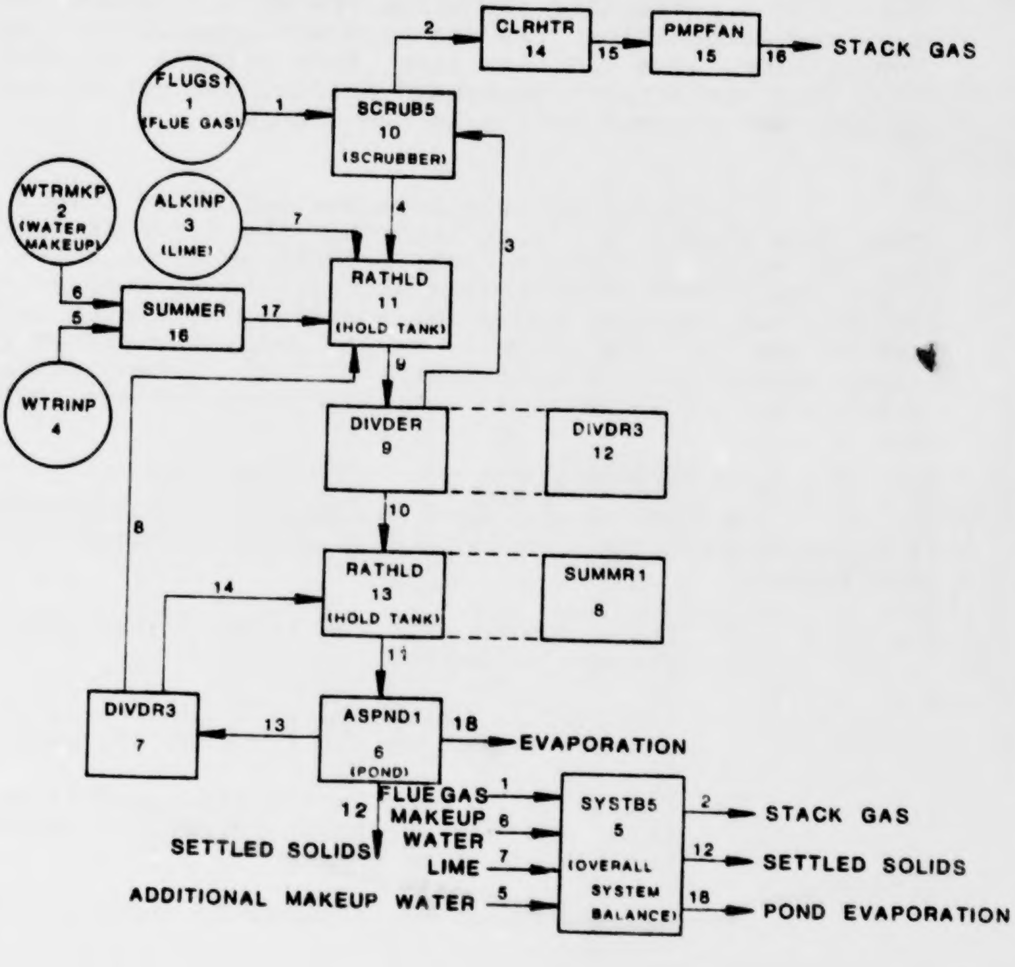
2.3 Scrubbing System

Each of the two 350 Mw units has three parallel scrubbing trains for removal of particulates and SO_2 from the flue gas. The basic flow scheme was described and sample analyses were presented in Section 2.1. This section of the appendix presents an analysis of the design scrubber operating conditions based on the sample analyses and operating data for the Colstrip plant. First, the simulation basis is presented, including a brief model description and a discussion of the input data used to simulate design conditions at Colstrip. Then the results of the simulations are compared to the sample results.

2.3.1 Simulation Basis

A process simulation of the Colstrip scrubbing system operating at design conditions was performed to characterize the system and to determine if a potential for water recycle/reuse exists with the present configuration. This section first briefly discusses the model, followed by a description of the operating parameters used as inputs to the model. A detailed discussion of the process model is included in Appendix E.

The process simulation flow scheme shown in Figure 2-3 was used to model the scrubbing system at Colstrip (see Figure 2-1 for process flow diagram). This model calculates



ORDER OF PROCESS CALCULATIONS:

1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 5, 6, 7, 8, 9, 16, (10, 11, 12,) 13, 14, 15 *

Figure 2-3. Colstrip scrubbing simulation flow scheme. (see Figure 2-1 for process flow diagram)

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all stream compositions and flow rates using precipitation rate kinetics for $CaSO_4 \cdot 2H_2O$ and $CaSO_3 \cdot \frac{1}{2}H_2O$, which are the solids formed in lime/limestone scrubbing systems, and various input parameters. These parameters characterize the operating conditions for a particular scrubbing system and include flue gas flow and composition, fly ash rate and composition, makeup water composition, lime addition rate, tank volumes, scrubber feed flow rate and percent suspended solids, percent oxidation in the system, and percent solids in the sludge.

Iterative calculations are performed around the scrubbing loop (boxes 10, 11, 12) through the scrubber vessel (SCRUB5) and the scrubber recycle tank (RATHLD) until relative saturations and stream compositions satisfy the rate equations. Then calculations are performed for ancillary equipment such as the reheat and fan requirements, and to determine stream compositions around the effluent tank (box 13). Makeup water requirements are calculated by an overall system balance (SYSTB5, box 5).

Several assumptions are inherent in performing this simulation with the model outlined above. These are enumerated below:

1) The scrubber exit gas is saturated with respect to water.

2) Equilibrium exists between CO_2 in the stack gas and liquor in the scrubber bottoms.

3) The scrubber bottoms and stack gas temperatures are the adiabatic saturation temperature of the flue gas.

4) All oxidation was assumed to occur in the scrubber.

5) All solids precipitation occurs in reaction vessels (subroutine RATHLD).

6) Ionic reactions taking place in the liquid phase are rapid and thus at equilibrium.

The data used as input to this model is presented in Table 2-4. Some of this data was obtained directly from MPC while some of it was calulated from MPC data or sample analyses.

TABLE 2-4. INPUT DATA FOR COLSTRIP SCRUBBING SIMULATION*

FLUE GAS	
Flow, m^3/hr	779,000
(ACFM)	(458,000)
Temperature, °C	141
(°F)	(291)
Composition, mole %	
SO_2	.079
CO_2	14.1
O_2	3.47
N_2	72.8
H_2O	9.52
Fly Ash Rate, kg/min	331
(lb/min)	(728)
SYSTEM PARAMETERS	
SO_2 Removal Efficiency, %	74
Oxidation, %	90
Particulate Removal Efficiency, %	99.6
Scrubber Feed Rate, ℓ/sec	963
(GPM)	(15,260)
Scrubber Slurry Solids, wt. %	12.
Recycle Tank Volume, m^3	380
(ft^3)	(13,370)
Effluent Tank Volume, m^3	43
(ft^3)	(1,520)
Effluent Tank Solids, wt. %	6.
Sludge, wt. % solids	50
MAKEUP WATER COMPOSITION, mg/ℓ	
Calcium	39.9
Magnesium	10.7
Sodium	40.3
Chloride	17.0
Carbonates (as $CO_3^{=}$)	6.0
Sulfates (as $SO_4^{=}$)	188.
Nitrate (as NO_3^{-})	1.4

* All flows and tank volumes are for each scrubber module.

The flue gas flow and composition were calculated from the coal composition and firing rate and the boiler excess air rate. The flue gas temperature entering the scrubber was obtained from MPC. Results of these calculations are presented in Appendix K.

All of the system parameters were supplied by MPC as design conditions. The makeup water composition was taken from the sample analyses after adjustment to minimize residual electroneutrality (see Appendix E). The fly ash composition was determined from the model by specifying the lime addition rate and adjusting the leachable content of the fly ash to match the species concentrations measured in the system. Leaching tests were performed for fly ash from MPC's Corette Plant which fires the same coal as Colstrip. Results of these studies are shown in Appendix D.

2.3.2 Simulation Results

This section describes the results from the simulation of design scrubber operations at Colstrip. Before the simulation was performed, a sample consistency calculation around the effluent tank was performed since gypsum relative saturations in the system varied from 1.0 to 1.38. Since all input and output streams around the effluent tank were sampled, this consistency check could be made. Table 2-5 shows the stream dissolved species concentrations and the results of the consistency calculation shown as a percent deviation defined as:

$$\frac{\Sigma \text{ species in} - \Sigma \text{ species out}}{(\Sigma \text{ species in} + \Sigma \text{ species out})/2} \times 100$$

A detailed description of the calculation technique is given in Appendix K.

As the results show in Table 2-5, the deviations for all species except carbonate and sulfite are acceptable. The excessive variation in sulfite is probably due to a small amount of oxidation occurring in the tank. Sulfite represents such a small portion of the total sulfur that 1-2% oxidation would adequately explain this inconsistency. The carbonate variation may be explained by CO_2 transfer between the process liquor and the atmosphere, and/or analytical errors.

TABLE 2-5. SAMPLE CONSISTENCY ERRORS AROUND EFFLUENT TANK AT COLSTRIP

Element	Stream Concentrations, mg/ℓ Pond recycle	 Scrubber blowdown	 Effluent tank	% Deviation*
Calcium	484	504	497	-1.9
Magnesium	1,550	5,050	2,075	+4.4
Sodium	305	458	315	+5.3
Potassium	13.1	21.9	15.5	-5.6
Chloride	70	129	74	+8.3
Carbonate	9.6	52.2	31.2	-58.3
Sulfite	400	300	100	+117.1
Total Sulfur	9,000	19,400	11,800	-8.5
Nitrate	130	161	118	+13.8

* Defined as $\frac{\Sigma \text{ in} - \Sigma \text{ out}}{(\Sigma \text{ in} + \Sigma \text{ out})/2} \times 100$

These calculations uphold the measured concentrations and therefore the calculated relative saturations. The low relative saturation (1.0) of $CaSO_4 \cdot 2H_2O$ in the scrubber recycle liquor indicates that some calcium or sulfate from the fly ash may be dissolving in the effluent tank causing the relative saturation to increase across the tank.

The results from the process simulation of design conditions are presented in Table 2-6. The calculated pH, suspended solids, relative saturations, and composition for the scrubber recycle slurry, effluent tank slurry, and pond recycle liquor are compared to the sample values for these streams.

The calculated pH of 4.98 for the recycle slurry compares well to the design value of 5 but under actual operation on the day of sampling, the pH was 3.9. The effluent tank pH's compared reasonably well but the pond recycle pH was higher in the sample than calculated. These pH variations indicate that the scrubbing system was not running under true steady-state conditions. This is due to the long residence time in the pond which makes the system time response to process changes quite slow.

The relative saturations in these three streams for $CaSO_4 \cdot 2H_2O$ were quite different in all cases. However, in one case, the recycle slurry, the sample value was lower than the calculated value but in the other two cases the calculated values were lower. Again, this can be explained by non-steady state operation and/or analytical errors.

The critical range of values for $CaSO_4 \cdot 2H_2O$ relative saturation for scale formation is 1.3-1.4. Gypsum relative saturations as high as 1.38 were found in the Colstrip scrubbing system indicating that operation at design conditions is very near scaling. Some nucleation may be occurring, but the erosive nature of the fly ash could be keeping vessel walls clean, or breaking up gypsum crystals to form very fine seeds to increase precipitation rates. The fly ash may also be providing nucleation sites for gypsum since no scale has been reported at Colstrip.

The stream compositions compared well in the recycle slurry with respect to magnesium, sodium and chloride. Calcium and sulfate concentrations were lower in the sampled stream,

TABLE 2-6. COLSTRIP SCRUBBING SIMULATION RESULTS FOR DESIGN CONDITIONS

Stream	Scrubber recycle slurry		Effluent tank		Pond recycle	
	Sample	Calculated	Sample	Calculated	Sample	Calculated
pH	3.9*	4.98	4.4	4.77	5.5	4.77
Suspended Solids, wt%	7.7**	12.6	1.36	6.0	neg.	0.0
Relative Saturations ***						
$CaSO_4 \cdot 2H_2O$	1.00	1.41	1.31	1.07	1.38	1.0
$CaCO_3$	1.9×10^{-5}	1.1×10^{-3}	1.5×10^{-6}	3.1×10^{-4}	2.2×10^{-5}	3.1×10^{-4}
Composition, mg/ℓ						
Calcium	504	733	497	542	484	498
Magnesium	5,050	5,285	2,075	5,690	1,550	6,010
Sodium	480	444	330	478	318	506
Chloride	129	117	74	126	70	133
Total Sulfur (as $SO_4^=$)	19,400	24,560	11,800	22,250	9,000	23,440
Sulfite (as $SO_3^=$)	300	3,560	100	3,650	400	3,750
Carbonate (as $CO_3^=$)	52.2	153	31.2	147	9.6	142
Nitrate (as NO_3^-)	161	9.6	118	10.3	130	10.9

* Design pH is 5

**Design is 12% solids

***Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$, and about 2.5 for $CaCO_3$ (see Appendix C) most probably due to reduced load and/or reduced SO_2 content in the gas from design conditions, resulting in a lower mass removal rate of sulfur from the gas.

The large magnesium variations in the other two streams may be explained by non-steady state, since magnesium concentrations throughout the system should be approximately the same at steady state.

The lower sample sulfite values are probably a result of increased oxidation over the design value of 90%. Lower SO_2 in the flue gas generally results in increased oxidation due to a higher oxygen to sulfur ratio.

One possibility for more efficient recycle/reuse at Colstrip might be to use a combination of cooling tower blowdown and river water or just river water as makeup to the scrubbing system without treatment. The effects of makeup water composition on scaling tendencies in the scrubbing system will be examined in Section 3.0.

3.0 TECHNICAL ALTERNATIVES

A modular approach to studying water recycle/reuse alternatives at Colstrip was used in that the major plant water system was divided into two subsystems to form separate process simulations. One subsystem consists of the cooling towers, with associated treatment facilities (where necessary), hold tanks, and condensers. The other subsystem consists of the combined SO_2 and particulate scrubbers including the disposal ponds. The studies for each subsystem will first be discussed separately. The effects of increasing the cycles of concentration versus treatment alternatives in the cooling towers and of using poorer quality makeup water (increased calcium and sulfate) are presented first. Then the effects of flue gas ash content, slurry percent solids, and makeup water composition on the scrubbing system operation are discussed. After investigating the water subsystems, possible alternatives for more efficient water recycle/reuse in the overall system are outlined.

3.1 Cooling Tower System

The existing operations simulations indicated that the towers were operating at about the maximum cycles of concentration without using slipstream softening. However, with slipstream treatment for calcium removal, the cycles may be increased resulting in a reduction in makeup water requirements for the cooling system. The amount of treatment required will depend on the circulating liquor calcium and sulfate concentrations. This section first presents a brief description of the simulation basis, followed by discussions of the results with respect to treatment alternatives and calcium and sulfate concentrations in the makeup water.

3.1.1 Simulation Basis

The process model used to simulate alternatives for cooling tower operation is identical to that used for existing operations. Slipstream softening was necessary to keep the $CaSO_4 \cdot 2H_2O$ relative saturation below the critical range for scaling of 1.3-1.4. Convergence criterion for this relative saturation is between 0.8 and 1.2 in the computer model.

A total of six simulations were performed for alternative cooling tower operations. One simulation was performed with the existing makeup water composition at 20 cycles of concentration. Another simulation was run to determine the maximum cycles using untreated makeup water. Four additional simulations at 20 cycles of concentration were run with variations in calcium and sulfate concentrations in the makeup water to determine slipstream treatment rates.

All of the alternative cooling tower simulations were performed for summer operation since under these conditions a maximum blowdown rate is achieved. Increased evaporation rates realized during the summer months necessitate an increase in blowdown rate over that required during the winter months to maintain a constant value for cycles of concentration. All values reported in this section refer to one unit unless specified otherwise.

The only changes in the input data for all of the alternative simulations are the values for cycles of concentration and makeup water composition.

3.1.2 Cooling Tower Makeup Treatment Alternatives

The results from the simulations with untreated water and with slipstream treatment are compared to the existing system operation with treated makeup water in Table 3-1. Column A represents operation without any softening of the makeup water or a slipstream of the circulating water. Column B represents the existing system with softening of the makeup water, and Column C represents operation with treatment of a slipstream for calcium removal.

Without any softening in the cooling tower loop, only 11 cycles of concentration can be obtained as compared to 13.5 cycles with pretreatment, before $CaSO_4 \cdot 2H_2O$ relative saturation approaches a value above 1.0. The makeup water rate for no treatment is slightly higher because of the lowered cycles of concentration. The lowered cycles also result in a small decrease in acid requirements and an increase in blowdown rate from 11.8 ℓ/sec (187 GPM) to 15.0 ℓ/sec (238 GPM) per tower. Approximately 820 kg/day (1800 lb/day) of $CaCO_3$ is removed from the makeup water per tower with pretreatment, allowing cycles to rise to 13.5.

When slipstream treatment is employed, cycles of concentration can be further increased. Slipstream treatment also only requires treatment of about 9 ℓ/sec (142 GPM) for 20 cycles whereas pretreatment requires that about 175 ℓ/sec (2770 GPM) of

TABLE 3-1. TREATMENT ALTERNATIVES FOR COLSTRIP COOLING TOWER OPERATION

	Treatment Method*		
	A	B	C
Cycles of Concentration	11.0	13.5	20.0
Makeup Water Rate, ℓ/sec	178	175	170
(GPM)	(2820)	(2770)	(2700)
Acid Addition Rate, kg/day**	127	152	161
(lb/day)	(279)	(334)	(354)
Treatment Rate, ℓ/sec	0	175	9.0
(GPM)	(0)	(2770)	(142)
Calcium Removal Rate, kg $CaCO_3$/day	0	820	1040
(lb/day)	(0)	(1800)	(2290)
Blowdown			
Flow, ℓ/sec	15.0	11.8	7.3
(GPM)	(238)	(187)	(115)
pH	7.5	7.2	7.6
Composition, mg/ℓ			
Calcium	631	534	587
Magnesium	117	143	212
Sodium	439	540	1450
Chloride	531	227	964
Carbonate (as $CO_3^=$)	22.3	6.5	25.5
Sulfate (as $SO_4^=$)	2140	2640	3930
Nitrate (as NO_3^-)	18.5	18.7	33.6
Temperature, °C	42.2	42.2	42.2
(°F)	(108)	(108)	(108)
Relative Saturations***			
$CaCO_3$	.92	.097	.86
$CaSO_4 \cdot 2H_2O$	.94	.93	1.02

* Method A = No treatment
Method B = Pretreatment (existing operations)
Method C = Slipstream treatment

** as 100% H_2SO_4

*** Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C) water be softened. The reason for this dramatic difference is that the slipstream of recirculating water is much more concentrated than the makeup water and the required calcium removal can be achieved by treating a smaller stream with a higher calcium level.

About 1040 kg/day (2290 lb/day) of $CaCO_3$ is removed from the slipstream of each tower at 20 cycles as compared to 820 kg/day (1800 lb/day) for pretreatment. Also, operating at 20 cycles of concentration results in a 38% reduction in blowdown flow from 11.8 ℓ/sec (187 GPM) with pretreatment (13.5 cycles) to 7.3 ℓ/sec (115 GPM) with slipstream treatment.

The level of slipstream treatment required will depend on the calcium and sulfate concentrations in the makeup water. Since these parameters may vary with time, the effects of calcium and sulfate concentrations on slipstream treatment were determined and are presented in the following sections.

3.1.3 Effects of Calcium Concentration in Makeup Water at 20 Cycles of Concentration

The results for the three simulations performed to determine the effects of makeup water calcium concentration on the magnitude of slipstream treatment are presented in Table 3-2. The calcium concentration in the makeup water was varied from 39.9 mg/ℓ to 80 mg/ℓ in the three runs made. The required slipstream treatment and calcium removal rates were calculated and increased as expected with increases in makeup calcium concentration. Slipstream rates varied from 2.8 ℓ/sec (45 GPM) to 13.2 ℓ/sec (210 GPM). Slipstream rate is plotted *versus* calcium concentration in the makeup water in Figure 3-1.

It should be noted here that this curve applies only to the makeup water composition considered. Variations in sulfate will definitely affect the slipstream rate and variations in other species' concentrations may cause significant changes due to chemical complexing. This curve is valid for the compositions considered and is presented to show trends in the system.

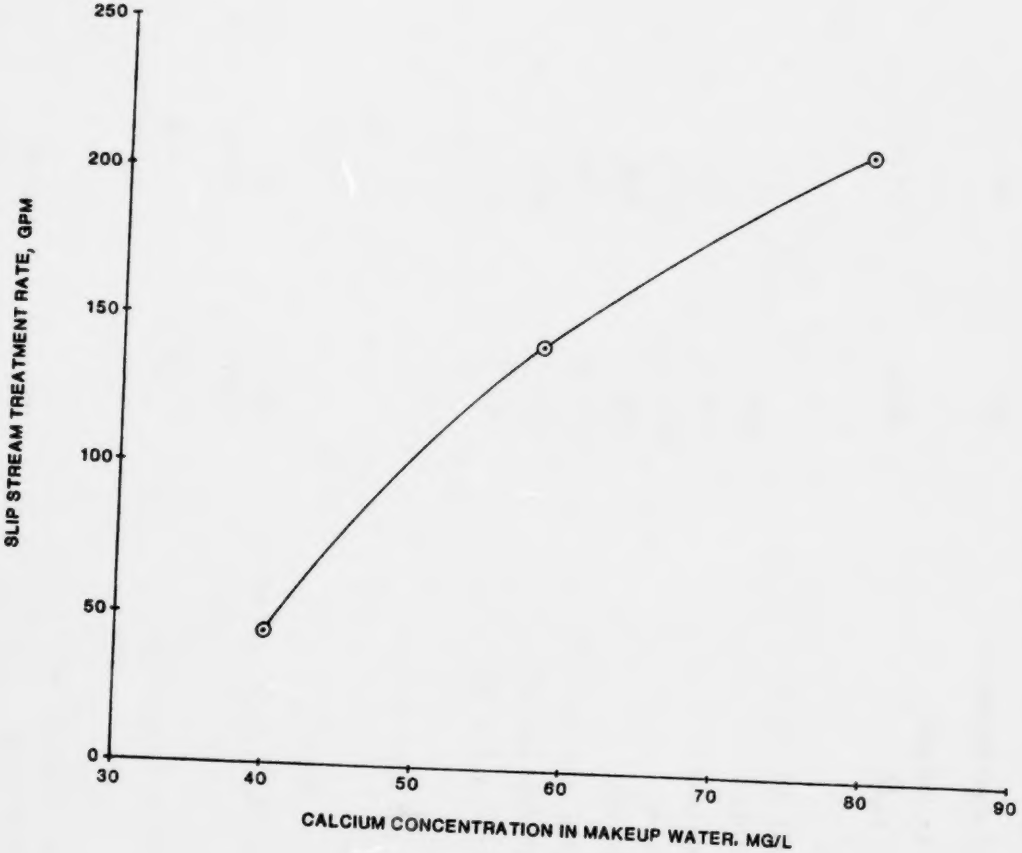


Figure 3-1. Slipstream rate as a function of makeup calcium concentration at Colstrip.

TABLE 3-2. SIMULATION RESULTS FOR CALCIUM VARIATIONS IN THE MAKEUP WATER AT COLSTRIP

	Low Calcium	Medium Calcium	High Calcium
Cycles of Concentration	20	20	20
Calcium in Makeup Water, mg/ℓ	39.9	57.9	80.0
Blowdown			
Composition, mg/ℓ			
Calcium	606	587	654
Magnesium	212	212	212
Sodium	1015	1450	1890
Chloride	336	964	1740
Carbonates (as $CO_3^=$)	21.6	25.5	24.8
Sulfates (as $SO_4^=$)	3910	3930	3950
Nitrates (as NO_3^-)	27.7	33.6	33.6
pH	7.7	7.6	7.6
Relative Saturation*			
$CaCO_3$	.98	.86	.96
$CaSO_4 \cdot 2H_2O$	1.13	1.02	1.05
Sulfuric Acid Rate, kg/day**	146	158	174
lb/day	(320)	(348)	(384)
Slipstream Rate, ℓ/sec	2.8	9.0	13.2
(GPM)	(45)	(142)	(210)
Calcium Removal Rate			
kg $CaCO_3$/day	341	1040	1725
(lb $CaCO_3$/day)	(749)	(2290)	(3800)

*Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C)

**100% H_2SO_4

3.1.4 Effect of Sulfate Concentration in Makeup Water at 20 Cycles of Concentration

Since the basis for defining slipstream treatment rates is the relative saturation of $CaSO_4 \cdot 2H_2O$, the concentration of the sulfate species in the makeup water will have a significant effect on these slipstream rates. As the sulfate increases, the relative saturation of gypsum will increase, necessitating additional calcium removal to prevent gypsum scale formation.

Two additional simulations were performed to quantify the differences in required slipstream treatment rates with changes in the makeup water sulfate concentration. The results from these two additional simulations along with the case using untreated makeup are shown in Table 3-3. The three values for sulfate considered were 125, 188, and 376 mg/ℓ. The case with 188 mg/ℓ represents the existing plant makeup water composition. Slipstream rates varied from 9.0 ℓ/sec (142 GPM) for the existing case (Simulation No. 4) to 4.9 ℓ/sec (77 GPM) for the lower sulfate concentration and 12.3 ℓ/sec (195 GPM) for the higher sulfate concentration.

The calculated slipstream rates are plotted *versus* sulfate concentration in the makeup water in Figure 3-2. Again, it should be noted that this curve applies only to the makeup water considered. Variations in calcium have been shown to affect slipstream rates in the previous section. In addition, variations in other species' concentrations may cause significant variations in slipstream rate due to the formation of ionic complexes in the water. If the magnesium bicarbonate process (TH-192) is used for slipstream treatment, the magnesium concentration in the system will increase and treatment requirements may be reduced. The effects of magnesium on $CaSO_4 \cdot 2H_2O$ relative saturation were presented in Appendix I. The curve in Figure 3-2, however, represent trends in the system as a function of makeup water sulfate concentration.

3.1.5 Summary of Cooling Tower Alternatives

The first set of simulations comparing treatment alternatives shows that with the use of slipstream softening, as opposed to the present pretreatment system, cycles of concentration may be increased in the cooling towers. Increasing the cycles from 13.5 (existing) to 20 reduces the blowdown rate from 11.8 ℓ/sec (187 GPM) to 7.3 ℓ/sec (115 GPM) and requires a slipstream rate of 9.0 ℓ/sec (142 GPM) for each tower.

Additional simulations were performed which showed the magnitude of effects of calcium and sulfate concentrations

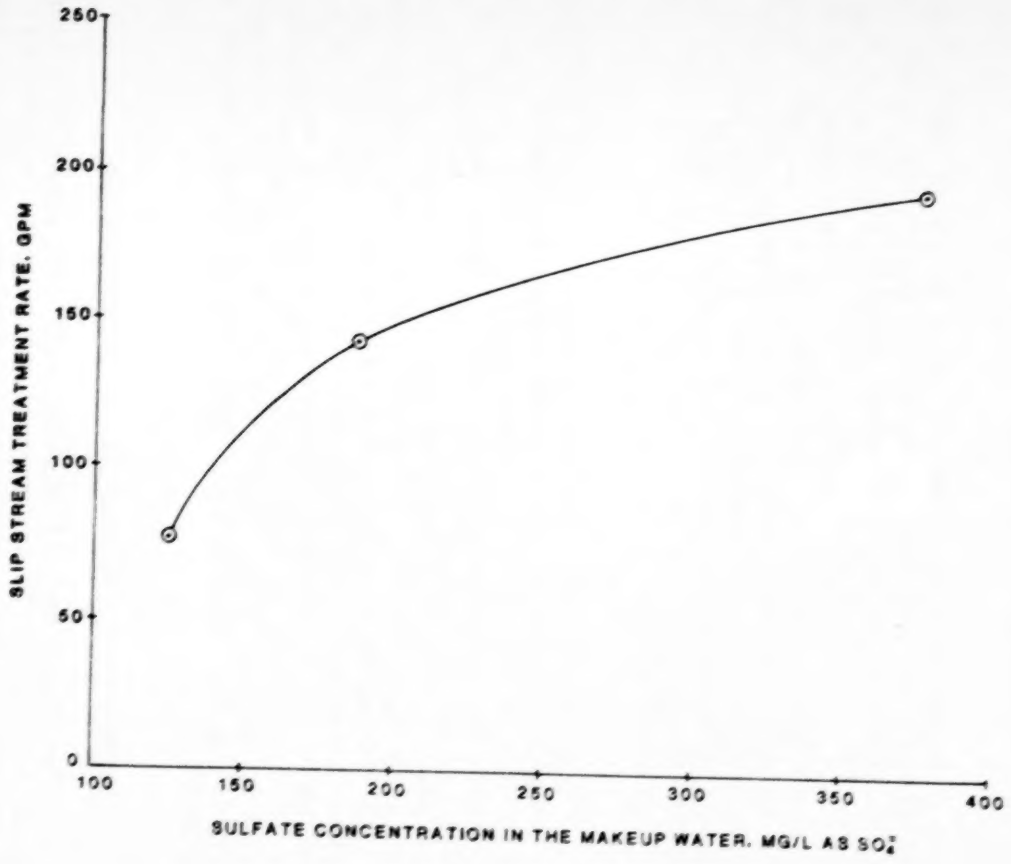


Figure 3-2. Slipstream rate as a function of makeup sulfate concentration at Colstrip.

TABLE 3-3. SIMULATION RESULTS FOR SULFATE VARIATIONS IN THE MAKEUP WATER AT COLSTRIP

	Low Sulfate	Medium Sulfate	High Sulfate
Cycles of Concentration	20.	20.	20.
Sulfate in Makeup Water, mg/ℓ as $SO_4^=$	125.	188.	376.
Blowdown			
Composition, mg/ℓ			
Calcium	751.	587.	501.
Magnesium	212.	212.	212.
Sodium	633.	1450.	3350.
Chloride	964.	964.	964.
Carbonates (as $CO_3^=$)	23.5	25.5	31.0
Sulfates (as $SO_4^=$)	2610.	3930.	7670.
Nitrates (as NO_3^-)	33.6	33.6	33.6
pH	7.5	7.6	7.8
Relative Saturations*			
$CaCO_3$	.87	.86	.90
$CaSO_4 \cdot 2H_2O$	1.09	1.02	1.03
Sulfuric Acid Rate, kg/day**	102.	158.	177.
(lb/day)	(225)	(348)	(389)
Slipstream Rate, ℓ/sec	4.9	9.0	12.3
(GPM)	(77)	(142)	(195)
Calcium Removal Rate			
kg $CaCO_3$/day	736.	1040.	1200.
(lb $CaCO_3$/day)	(1620)	(2290)	(2640)

*Critical values, above which scale potential exists, are 1.3-1.4 for $CaSO_4 \cdot 2H_2O$ and about 2.5 for $CaCO_3$ (see Appendix C)

**100% H_2SO_4

in the makeup water on slipstream treatment rate. Graphs of these effects showed that calcium had a greater effect on the rate than did sulfate since the slope of the treatment rate versus concentration plot for calcium was steeper than that for sulfate. Doubling the calcium concentration increased the treatment rate about 370% from 2.8 ℓ/sec (45 GPM) to 13.2 ℓ/sec (210 GPM), whereas doubling the sulfate concentration only increased the treatment rate about 37%, from 9.0 ℓ/sec (142 GPM) to 12.3 ℓ/sec (195 GPM).

Operating the cooling towers at higher cycles of concentration may cause species besides gypsum and calcium carbonate to become supersaturated and possibly form scale. Table 3-4 shows relative saturations for silica and phosphate solids in the cooling tower blowdown at 20 cycles. The silica solid with the largest relative saturation is SiO_2 with a value of .12 which is well below saturation. The highest magnesium-silica solid relative saturation is for $Mg(SiO_2)_3(OH)_2$ (sepiolite) with a value of 0.20.

TABLE 3-4. RELATIVE SATURATIONS OF SCALE-FORMING SPECIES FOR 20 CYCLES WITH EXISTING MAKEUP WATER AT COLSTRIP*

Species	Relative Saturation
$Ca(OH)_2$	9.6×10^{-10}
$CaCO_3$	0.60
$CaSO_4 \cdot 2H_2O$	1.13
$CaHPO_4$	0.015
$Ca_3(PO_4)_2$	5.4×10^{-4}
$Mg(OH)_2$	2.5×10^{-4}
$MgCO_3$	6.7×10^{-5}
SiO_2	0.12
$Mg_2Si_3O_5(OH)_6$	6.1×10^{-5}
$Mg_3Si_2O_5(OH)_4$	0.012
$Mg(SiO_2)_3(OH)_2$	0.20
CaH_2SiO_4	1.8×10^{-4}
$Ca(H_2SiO_4)_2$	5.2×10^{-4}

*This simulation required an acid addition rate of 354 lb H_2SO_4/day and a slipstream treatment rate for calcium removal of 142 GPM.

3.2 Ash Handling (Particulate and SO_2 Scrubbing) System

The simulation performed for design conditions in the scrubbing system indicated the relative saturation of gypsum in the system at steady state is at the upper level of the critical range for scale formation of 1.3-1.4. Although increased recycle/reuse cannot be employed in the scrubbing system since the system is already at zero discharge, more efficient use of water in the overall plant water system may be achieved by using a different makeup water source in the scrubbers.

This section examines the effects of makeup water as well as flue gas ash content and slurry percent solids on the scale-free operation of the Colstrip scrubbing system. First, a brief description of the simulation basis is given. Then discussions of the effects of flue gas ash content, slurry percent solids, and makeup water composition on scrubber operation are presented.

3.2.1 Simulation Basis

The process model used to examine the effects of operating parameters on scrubber operation is identical to that used for design operation.

Four additional simulations were performed. One was run with all parameters identical except the flue gas ash content was lowered by 30% to represent operation with coal of a lesser ash content. Another simulation was performed with the base case data except the scrubber recycle suspended solids were reduced to about 7.5% as opposed to the design value of 12%. Finally, two additional simulations were performed with cooling tower blowdown and untreated water as makeup sources to the scrubbers.

3.2.2 Effects of Flue Gas Ash Content

The simulation results for reduced flue gas ash content are compared to the design operation results in Table 3-5. The fly ash in the flue gas entering the scrubber was lowered from the design rate of 331 kg/min (728 lb/min) to 230 kg/min (505 lb/min). The pH of the recycle slurry was maintained at 5 as this is the design value. The lower ash content in the flue gas lowers the fraction of the recirculating solids which is inert ash, thereby increasing the fraction of the solids which is gypsum. Table 3-5 shows that the portion of the slurry solids which is $CaSO_4 \cdot 2H_2O$ increased from 38.9% to 47.2%.

TABLE 3-5. EFFECT OF FLUE GAS ASH CONTENT ON COLSTRIP SCRUBBER OPERATION

	Simulation No.	
	1 (Design Conditions)	2
Flue Gas Ash Flow, kg/min	331	230
(lb/min)	(728)	(505)
Scrubber Recycle Slurry		
pH	4.98	5.18
Liquor Composition, mg/ℓ		
Calcium	733	715
Magnesium	5,285	4,267
Sodium	444	448
Chloride	117	132
Carbonates (as $CO_3^=$)	153	156
Sulfates (as $SO_4^=$)	21,000	17,800
Sulfite (as $SO_3^=$)	3,560	2,135
Nitrate (as NO_3^-)	9.6	10.9
Solid Composition, wt %		
$CaSO_4 \cdot 2H_2O$	38.9	47.2
Inert (ash)	57.3	47.8
$CaSO_3 \cdot 1/2H_2O$	3.8	5.0
Relative Saturation*		
$CaSO_4 \cdot 2H_2O$	1.41	1.37

*The critical value, above which scale potential exists, is 1.3-1.4 for $CaSO_4 \cdot 2H_2O$

The increase in recirculating gypsum solids provides more precipitation sites, allowing more efficient solids formation and, therefore, a lower gypsum relative saturation in the liquor. The simulation of lower ash content in the flue gas predicted a reduction in gypsum relative saturation from 1.41 to 1.37. This means that operation with less than the design ash rate will be more conducive to nonscaling operation, and that operation with a higher ash rate may cause scaling problems. However, the presence of erosive ash may cause the gypsum crystals to be broken up, providing more precipitation sites and, therefore, counteract to some extent the increased scale potential caused by higher ash content in the recirculating solids.

3.2.3 Effects of Slurry Solids Content

The design value for slurry solids content is 12%. The slurry solids content will have an effect on scrubber operation since these recirculating solids provide the precipitation sites for $CaSO_4 \cdot 2H_2O$ solid formation in the reaction tank. The results of the simulation performed at about 7.5% solids are compared to the design operation (12% solids) results in Table 3-6.

TABLE 3-6. EFFECT OF SLURRY SOLIDS CONTENT ON COLSTRIP SCRUBBER OPERATION

	Simulation No.	
	1 (Design Conditions)	2
Flue Gas Ash Rate, kg/min	331.	331.
(lb/min)	(728)	(728)
Scrubber Recycle Slurry		
Suspended Solids, wt. %	12.6	7.6
pH	4.98	5.09
Liquor Composition, mg/ℓ		
Calcium	733.	897.
Magnesium	5,285.	5,590.
Sodium	444.	469.
Chloride	117.	124.
Carbonate (as $CO_3^=$)	153.	167.
Sulfate (as $SO_4^=$)	21,000.	22,300.
Sulfite (as $SO_3^=$)	3,560.	3,930.
Nitrate (as NO_3^-)	9.6	10.2
Solid Composition, wt. %		
$CaSO_4 \cdot 2H_2O$	38.9	38.7
Inert (ash)	57.3	57.9
$CaSO_3 \cdot \frac{1}{2}H_2O$	3.8	3.4
Relative Saturation*		
$CaSO_4 \cdot 2H_2O$	1.41	1.73

*The critical value, above which scale potential exists, is 1.3-1.4 for $CaSO_4 \cdot 2H_2O$

The solids composition remained essentially constant, but the gypsum relative saturation rose from 1.41 to 1.73, which is significantly above the critical range for scale formation of 1.3-1.4. This rise in relative saturation is a result of the decrease in gypsum solids circulating around the scrubbing loop which decreases the number of precipitation sites and, therefore, the precipitation rate. Continuous operation at lower solids content will most likely cause some scale formation at Colstrip.

3.2.4 Effects of Makeup Water Composition

Two simulations were performed to determine the effects of makeup water composition on scrubber operation. One was run with untreated makeup water and one with existing cooling tower blowdown as makeup water. The results from these two simulations (Nos. 3 & 5) are compared to design conditions in Table 3-7. The differences between using treated makeup (design operation) and using untreated makeup (Case 3) are hardly noticeable. An increase in calcium level in the makeup water did not have a significant effect on liquor composition, solid composition, or gypsum relative saturation in the system. This is due to the fact that the calcium added with the makeup water to the reaction tank represents only a small portion (about .07% for Case 3) of the total liquid phase calcium present in the tank. In the overall system, the calcium added through the makeup water represents 0.4% of the total calcium entering the system for Simulation 3 (untreated makeup water).

The last column in Table 3-7 shows the results from the simulation with existing cooling tower blowdown as makeup water. Although the composition of the scrubber recycle liquor changed, the relative saturation of $CaSO_4 \cdot 2H_2O$ did not change appreciably. The more concentrated cooling tower blowdown causes the concentrations in the scrubbing system to be increased. However, in the more concentrated liquor, more chemical complexing is occurring, and the activity coefficients of the dissolved species are affected such that the relative saturation of gypsum is virtually unchanged. The increase in chlorides from 117 mg/ℓ to 1560 mg/ℓ should not make the chloride level high enough to cause corrosion problems (UH-007). Problems could possibly be encountered in the mist eliminators if cooling tower blowdown is used. However, a combination of river water and cooling tower blowdown or just river water could perhaps be used as mist eliminator wash. Cooling tower blowdown may be saturated with respect to $CaSO_4 \cdot 2H_2O$ if the towers are operated at high cycles of concentration and therefore could cause gypsum scaling problems in the demister if used for demister wash.

TABLE 3-7. EFFECTS OF MAKEUP WATER COMPOSITION ON COLSTRIP SCRUBBER OPERATION

	Simulation No.		
	1 (Design Operation)	3	5
Makeup Water Source*	Treated Makeup	Untreated Makeup	Cooling Tower Blowdown
Flue Gas Ash Rate, kg/min	331	331	331
(lb/min)	(728)	(728)	(728)
Scrubber Recycle Slurry			
Suspended Solids, wt %	12.6	12.6	12.6
pH	4.98	4.97	5.04
Liquor Composition, mg/ℓ			
Calcium	733	740	686
Magnesium	5,285	5,284	6,190
Sodium	444	444	3,870
Chloride	117	335	1,560
Carbonate (as $CO_3^{=}$)	153	154	150
Sulfate (as $SO_4^{=}$)	21,000	20,700	29,400
Sulfite (as $SO_3^{=}$)	3,560	3,552	3,700
Nitrate (as NO_3^-)	9.6	11.7	128
Solid Composition, wt %			
$CaSO_4 \cdot 2H_2O$	38.9	38.9	39.9
Inert (ash)	57.3	57.2	56.3
$CaSO_3 \cdot 1/2H_2O$	3.8	3.9	3.8
Relative Saturation**			
$CaSO_4 \cdot 2H_2O$	1.41	1.41	1.42

* Makeup Waters, mg/ℓ	Treated Makeup	Untreated Makeup	Cooling Tower Blowdown (13.5 cycles)
Calcium	39.9	57.9	533.7
Magnesium	10.7	10.7	143.1
Sodium	40.3	40.3	539.5
Chloride	17.0	48.7	227.4
Carbonate (as $CO_3^{=}$)	6.0	17.3	6.5
Sulfate (as $SO_4^{=}$)	188.	188.	2,644.2
Nitrate (as NO_3^-)	1.4	1.7	18.7
Relative Saturation of $CaSO_4 \cdot 2H_2O$	0.03	0.04	0.93

**The critical value, above which scale potential exists, is 1.3-1.4 for $CaSO_4 \cdot 2H_2O$

3.2.5 Summary of Scrubbing Alternatives

The first two simulations characterized the system response to flue gas ash content and slurry percent solids. As the ash rate increases, the fraction of the circulating solids that is gypsum decreases, and the relative saturation of $CaSO_4 \cdot 2H_2O$ increases. As the percent solids in the circulating liquor decreases, the amount of circulating gypsum solids decreases and the relative saturation of $CaSO_4 \cdot 2H_2O$ increases. Burning a coal of significantly higher ash content or operating the system at low solids in the recycle loop may cause scaling problems in the scrubbers at Colstrip.

The last set of simulations showed that the use of either untreated water or cooling tower blowdown as makeup to the scrubbing system does not have a significant impact on the scaling tendency of the system. The use of cooling tower blowdown will increase the total dissolved solids and chloride corrosion problems (UH-007). The use of cooling tower blowdown as mist eliminator wash exclusively could cause scaling problems but dilution of the cooling tower blowdown with river water could possibly control scaling in the mist eliminators.

3.3 Combined System Alternatives

From the results of these simulations, cycles of concentration can be increased through the use of slipstream softening in the cooling system, and cooling tower blowdown and raw makeup water may be used in the scrubbing system. Two technical alternatives are outlined here. The economics associated with these alternatives are presented in Section 4.0.

The first alternative involves using treated water for cooling tower makeup as is presently done. A portion of the cooling tower blowdown could be used as feed to one brine concentrator as needed for boiler makeup. The remainder of the cooling tower blowdown can then be used in combination with untreated river water as makeup to the scrubbers. The makeup water requirements for this alternative will be the same as the present amount, but softening requirements will be reduced and only one brine concentrator is required.

The second alternative involves using raw river water as cooling tower makeup and operating the towers at 20 cycles of concentration with slipstream softening. As in Alternative 1, a portion of the cooling tower blowdown can be used to feed one brine concentrator as needed for boiler makeup, and the remainder can be used in combination with untreated water as scrubbing makeup. In this case the overall plant water requirements are unchanged but only one brine concentrator is used. The flow to the softener is decreased dramatically but the chemical requirements are increased due to an increase in the calcium removal rate.

Rough economic estimates are presented in the next section so that these two alternatives may be compared.

4.0 ECONOMICS

This section provides rough cost estimates for implementing each of the two alternatives discussed in the previous section. Both rough capital costs and operating costs are presented. The assumptions and techniques used in calculating these costs are briefly outlined. It should be emphasized here that these economics are only rough estimates for comparative purposes. It should also be noted that the following costs are concerned with using the existing equipment at Colstrip and do not reflect any savings which could have been realized if more effective water recycle/reuse had been used at Colstrip initially.

A capital cost summary for the two alternatives is shown in Table 4-1. The system modifications for Alternative 1 include piping for using water before softening as scrubber makeup and for using cooling tower blowdown as scrubber makeup. Also included is additional pumps for transporting the cooling tower blowdown to the scrubbing system. Alternative 2 modifications include all of the changes for Alternative 1 plus additional pumps and piping to convert to slipstream softening instead of pretreatment in the cooling tower system.

Four-inch carbon steel pipe with average fittings, flanges, shop coating, and wrapping was assumed for cooling tower blowdown and slipstream softening streams. Six-inch pipe was used for untreated water to the scrubbers. A labor to material ratio of 0.8 was used to determine installation costs. Engineering costs (direct and indirect) were assumed to be 7.2% of the combined labor and material cost (GU-075).

Cast steel pumps with electric motor drivers were used for cooling tower blowdown and slipstream softening. A labor material ratio of 0.36 was used for installation costs. Engineering was assumed to be 10% of the combined labor and material cost (GU-075).

All pump and piping costs were upgraded from 1970 dollars to 1976 dollars using a factor of 1.56 (based on Chemical Engineering Index).

An operating cost summary for the two alternatives is presented in Table 4-2. Negative operating costs in this table represents savings over existing operation. In the first

TABLE 4-1. CAPITAL COSTS FOR WATER RECYCLE/REUSE ALTERNATIVES AT COLSTRIP

Item	Alternative One (1976 dollars)	Alternative Two (1976 dollars)
Piping for raw water to scrubbers	5,000	5,000
Piping for cooling tower blowdown to scrubbers	60,000	60,000
Additional pumps and drivers for cooling tower blowdown	64,000	64,000
Piping to convert to slip stream softening	--	25,000
Additional pumps and drivers for slip stream softening	--	69,000
Contingency (20%)	26,000	45,000
Contractual Fees (3%)	4,000	7,000
Total	159,000	275,000

TABLE 4-2. OPERATING COSTS FOR WATER RECYCLE/ REUSE ALTERNATIVES AT COLSTRIP[1]

Item	Alternative One (1976 dollars/yr)	Alternative Two (1976 dollars/yr)
Lime for softening ($35/ton)	-1,000	1,000
Brine concentrator operation ($2/1000 gal)[2]	-260,000	-260,000
Capital Charges (15% per year)[3]	24,000	42,000
Total	-237,000	-217,000
(mils/kw-hr)	(-.046)	(-.044)

[1] Based on 80% load factor

[2] LE-239

[3] MC-136

alternative a savings is shown for softening lime requirements. This is a result of the decrease in softener flow since the scrubber makeup water is not softened in this alternative.

Alternative 2, on the other hand, shows an additional operating expense of $1,000/yr for softening. This is due to an increase in the required calcium removal rate in the cooling tower system since the towers are operating at 20 cycles of concentration in Alternative 2. The use of slipstream softening in this alternative allows treating a small, concentrated stream as opposed to treating a large, dilute stream as is presently done. If slipstream softening had been designed into the cooling system initially a capital cost savings for softening could have been realized due to the much smaller equipment required. The costs reported here, however, are based on using the existing softening equipment at Colstrip.

An operational savings is shown for brine concentrator operation for both alternatives in Table 4-2. This estimate is based on an operating cost of $2/1,000 gal (LE-239). The savings results from reducing the brine concentrator feed rate from about 25 ℓ/sec (400 GPM) to 5.7 ℓ/sec (90 GPM). Only one of the two brine concentrators is used in these alternatives. The extra unit will insure that boiler feed water is always available when the unit is running. If this more effective cascading of water at Colstrip had been used initially, only one brine concentrator with 9.5 ℓ/sec (150 GPM) capacity would be required as opposed to the two 12.6 ℓ/sec (200 GPM) units being operated presently. This represents a capital cost savings that could have been realized of about $1.9 million based on $7,750/GPM (LE-239). The economics reported here do not reflect this savings but only consider what can be done with the existing equipment.

The last operating expense shown in Table 4-2 is capital charges. These costs were estimated as 15% (MC-136) of the capital investment shown in Table 4-1 for each alternative based on a 30-year lifetime. The net operating costs do not vary greatly between alternatives. The major difference is a result of the increased capital charges for slipstream softening equipment. In both cases, a net savings was calculated due to the large savings in brine concentrator operation.

APPENDIX K

POWER PLANT DATA REDUCTION

1.0 APS FOUR CORNERS STATION

Much of the data required to study the water use system at Four Corners were supplied directly by Arizona Public Service (APS). Some of the information was calculated. This section presents the required calculations.

1.1 Four Corners Scrubbing System

Calculations were performed to estimate the particulate removal efficiency, the SO_2 oxidation rate, and the flue gas composition at Four Corners. A study was performed to estimate the reactivity of the ash produced at Four Corners. These calculations and the results of the batch dissolution studies are presented in this subsection. These results were used to simulate the scrubbing system at Four Corners.

1.1.1 Four Corners Scrubbing System Particulate Removal Efficiency

Inlet Loading

Unit 1 & 2 = 332 lb/min/train x 4 trains = 1328 lb/min

Unit 3 = 408 lb/min/train x 2 trains = 816 lb/min

Outlet Loading

Unit 1 & 2 = 1.08 lb/min/train x 4 trains = 4.32 lb/min

Unit 3 = 1.37 lb/min/train x 2 trains = 2.74 lb/min

Efficiency (Eff)

$$\text{Unit 1 \& 2 Eff} = \frac{1328 - 4.32}{1328} \times 100 = 99.67\%$$

$$\text{Unit 3 Eff} = \frac{816 - 2.74}{816} \times 100 = 99.66\%$$

$$\text{Average Eff} = 99.67\%$$

1.1.2 Four Corners SO_2 Oxidation Rate

Scrubber 1A Liquor

Total Sulfur = 28.6 mmoles/ℓ

$SO_3^{=}$ = 0.10 mmoles/ℓ

$$\% \text{ Oxidation} = \frac{28.6 - 0.1}{28.6} \times 100 = 99.65\%$$

Scrubber 3A Liquor

Total Sulfur = 30.5 mmoles/ℓ

$SO_3^{=}$ = 0.75 mmoles/ℓ

$$\% \text{ Oxidation} = \frac{30.5 - 0.75}{30.5} \times 100 = 97.54\%$$

Average % Oxidation = 98.6%

1.1.3 Four Corners Flue Gas Composition Calculations

Coal Composition

Component	wt%
C	52.62
H	3.81
S	0.69
N	1.19
O	9.02
H_2O	11.69
Ash	20.98
Total	100.00

Btu/lb = 9300

Basis: 100 lb coal; 3% O_2 in boiler exit gas

Coal in Component	lbs	lb moles
C	52.62	4.385
H	3.81	3.81
S	0.69	0.02156
N	1.19	0.085
O	9.02	0.5638
H_2O	11.69	0.6494

$$\text{Required moles of } O_2 = 4.385 + \tfrac{1}{4}(3.81) + .02156 - \tfrac{1}{2}(.5638)$$
$$= 5.077 \text{ lb moles}$$

$$\text{Nitrogen out} = \frac{79}{21}\,(O_2 \text{ in air}) + \tfrac{1}{2}(.085)$$

$$\text{Oxygen out} = O_2 \text{ in air} - 5.077$$

$$\text{Flue Gas Out (lb moles)} = F = \text{moles } CO_2 + \text{moles } H_2O + \text{moles } SO_2 + \text{moles } N_2 + \text{moles } O_2$$

$$F = 4.385 + 2.554 + 0.02156 \left[\frac{79}{21}\,(O_2 \text{ in air}) + \tfrac{1}{2}(.085)\right] + \left[O_2 \text{ in air} - 5.077\right]$$

$$\text{Moles } O_2 \text{ out} = O_2 \text{ in air} - 5.077 = .03F$$

so, O_2 in air = .03F + 5.077

Substituting into above equation for gas flow and solving:

F = 30.67 lb moles

Moles O_2 out = (.03)(30.67) = 0.920 lb moles

$$\text{Moles } N_2 \text{ out} = \frac{79}{21}\left[.03(30.67) + 5.077\right] + \tfrac{1}{2}(0.85) = 22.6 \text{ lb moles}$$

These calculations result in the following gas composition exiting the boiler

Component	moles	mole%
CO_2	4.385	14.39
H_2O	2.554	8.38
SO_2	0.02156	0.0707
N_2	22.60	74.15
O_2	0.920	3.02

If 10% leakage is occurring in air preheater there are an additional 3.07 moles of air in the gas

Moles N_2 = .79 (3.07) = 2.4

Moles O_2 = .21 (3.07) = 0.64

Gas Composition Entering Scrubber

Component	moles	mole%
CO_2	4.385	13.08
H_2O	2.554	7.62
SO_2	0.2156	0.0643
N_2	25.00	74.59
O_2	1.560	4.65

1.1.4 Batch Dissolution Results with Fly Ash From Four Corners

Fly Ash Composition

Component	wt%
P_2O_5	0.35
SiO_2	56.44
Fe_2O_3	3.80
Al_2O_3	27.98
TiO_2	1.06
CaO	3.04
MgO	1.19
SO_3	0.55
K_2O	0.77
Na_2O	2.32
Unidentified	2.50
Total	100.00

Existing operations: (Ash dissolution from data in ash leaching results); pH = 3.0, 2.0 wt % solids in slurry.

The calculations below show the results of the leaching studies. The actual values used in existing operations simulations were adjusted slightly to obtain the scrubber blowdown pH observed. The values used were 44% for CaO dissolution and 1.5% for MgO as compared to the respective calculated values of 41.7% and 1.1%.

CaO Dissolution

$$\frac{4.52 \text{ mmoles Ca dissolved}}{\text{liter}} \times \frac{40 \text{ mg Ca}}{\text{mmole Ca}} \times \frac{.1 \text{ liter}}{2 \text{ g ash}} = \frac{9.05 \text{ mg Ca dissolving}}{\text{g ash}}$$

$$\frac{9.05 \times 10^{-3} \text{ g Ca}}{\text{g ash}} \times \frac{56 \text{ g CaO}}{40 \text{ g Ca}} \times \frac{\text{g ash}}{0.0304 \text{ g CaO total}} \times 100 = \text{41.7\% CaO dissolving}$$

RESULTS OF CHEMICAL ANALYSIS FROM LEACHING OF ASH SAMPLES AT CONSTANT pH FOR FOUR CORNERS POWER STATION

	Prec. Ash[1] pH 3.0 (mmole/ℓ)[6]	Prec. Ash[2] pH 6.0 (mmole/ℓ)[6]	Prec. Ash[3] pH 8.5 (mmole/ℓ)[6]	Prec. Ash[4] pH 3.0 (mmole/ℓ)[7]	Prec. Ash[5] pH 8.5 (mmole/ℓ)[7]
Calcium	15.5	13.4	11.7	4.52	3.02
Magnesium	.23	.10	.07	.07	.01
Sodium	.52	.48	.48	.12	.08
Potassium	.12	.06	.04	.04	<.02
Sulfate	1.2	.31	.56	.08	.01

[1] Maintained pH of 3.0 by adding HCl.

[2] Maintained pH of 6.0 by adding HCl.

[3] Maintained pH of 8.5 by adding HCl.

[4] Maintained pH of 3.0 by adding HCl.

[5] Maintained pH of 8.5 by adding HCl.

[6] All values represent mmole/ℓ of soluble species in leachate after 14 grams of ash were leached in 186 grams of water at constant pH.

[7] All values represent mmole/ℓ of soluble species in leachate after 4 grams of ash were leached in 196 grams of water at constant pH.

MgO Dissolution

$$\frac{0.07\ \text{mmoles Mg dissolved}}{\text{liter}} \times \frac{24.3\ \text{mg Mg}}{\text{mmole Mg}} \times \frac{0.1\ \text{liter}}{2\ \text{g ash}} = \frac{0.08\ \text{mg dissolving}}{\text{g ash}}$$

$$\frac{8.\ \times 10^{-5}\ \text{g Mg dissolving}}{\text{g ash}} \times \frac{40.3\ \text{g MgO}}{24.3\ \text{g Mg}} \times \frac{\text{g ash}}{0.0119\ \text{g MgO total}} \times 100 =$$

1.1 % MgO dissolving

Alternatives: (Ash dissolution from data in ash leaching results); pH = 6.0, 7.0 wt. % solids in slurry.

CaO Dissolution

$$\frac{13.4\ \text{mmoles Ca dissolved}}{\text{liter}} \times \frac{40\ \text{mg Ca}}{\text{mmole Ca}} \times \frac{.1\ \text{liter}}{7\ \text{g ash}} =$$

$$\frac{7.66\ \text{mg Ca dissolving}}{\text{g ash}}$$

$$\frac{7.66 \times 10^{-3}\ \text{g Ca}}{\text{g ash}} \times \frac{56\ \text{g CaO}}{40\ \text{g Ca}} \times \frac{\text{g ash}}{.0304\ \text{g CaO total}} \times 100 =$$

35.4% CaO dissolving

MgO Dissolution

$$\frac{.10\ \text{mmoles Mg dissolved}}{\text{liter}} \times \frac{24.3\ \text{mg Mg}}{\text{mmole Mg}} \times \frac{.1}{7\ \text{g ash}} =$$

$$\frac{.035\ \text{mg Mg dissolving}}{\text{g ash}}$$

$$\frac{3.5 \times 10^{-5}\ \text{g Mg dissolving}}{\text{g ash}} \times \frac{40.3\ \text{g MgO}}{24.3\ \text{g Mg}} \times \frac{\text{g ash}}{0.119\ \text{g MgO total}} \times 100 =$$

0.5% MgO dissolving

2.0 GPC PLANT BOWEN

Much of the data required to study the water use system at Bowen were supplied directly by Georgia Power Company (GPC). Some of the information was calculated. This section presents the calculations which were required to perform simulations of the cooling tower and ash sluicing systems.

2.1 Bowen Cooling Towers

Estimates of the ambient air composition and temperature were calculated for the cooling tower simulations. These calculations are presented below.

2.1.1 Climatological Data

Month	Wet Bulb Temp.,°F	Dry Bulb Temp.,°F	Relative Humidity,%
Dec. 74	41	44	75
Jan. 75	42	47	71
Feb.	43	47	73
Mar.	44	50	66
Apr.	52	60	61
May	64	70	74
Jun.	68	74	73
Jul.	71	75	83
Aug.	72	77	84
Sep.	65	69	81
Oct.	58	62	77
Nov.	48	54	69

Winter Average Conditions (Dec., Jan., Feb.)

Wet Bulb Temp.	42°F
Dry Bulb Temp.	46°F
Relative Humidity	73%

Summer Average Conditions (Jun., Jul., Aug.)

Wet Bulb Temp.	70°F
Dry Bulb Temp.	75°F
Relative Humidity	80%

Air Flow (Example Calculation) - Winter

Cooling Tower 3 or 4:

Design flow = 100 x 10^6 lb/hr (wet bulb temp. = 25°F, 75% relative humidity)

Water content = 0.0024 lb H_2O/lb bone dry air (BDA)

$$\text{lb BDA} = \frac{100 \times 10^6}{1.0024} = 9.976 \times 10^7 \text{ lb/hr}$$

For wet bulb temp. = 42°F, 73% relative humidity

Water content = 0.0047 lb H_2O/lb BDA

Total Flow = 1.0047 x 9.976 x 10^7 = 100.2 x 10^6 lb/hr

$$\text{ACFM} = \frac{100.2 \times 10^6 \text{ lb}}{\text{hr}} \times \frac{\text{hr}}{60 \text{ min}} \times \frac{\text{lb-mole}}{29 \text{ lb}} \times \frac{359 \text{ scf}}{\text{lb-mole}} \times \frac{506\,°\text{R}}{492\,°\text{R}}$$

$$= 2.12 \times 10^7 \text{ ACFM}$$

Air Composition (Example Calculation) - Winter

Basis:	1 lb BDA	mole fraction
N_2	.0272 lb moles	0.7845
O_2	.0072	0.2077
CO_2	1.03×10^{-5}	0.0003
H_2O	2.61×10^{-4}	0.0075
	.034671 lb moles	1.0000

$$\text{moles } H_2O = \frac{.0047 \text{ lb } H_2O}{18 \text{ lb/lb-mole}} = 2.61 \times 10^{-4} \text{ lb moles } H_2O\text{/lb BDA}$$

$$\text{moles } N_2 = \frac{1 \text{ lb BDA}}{29 \text{ lb/lb-mole}} = .79 \frac{\text{moles } N_2}{\text{total moles}} =$$

0.0272 lb moles N_2/lb BDA

$$\text{moles } O_2 = \frac{1 \text{ lb BDA}}{29 \text{ lb/lb-mole}} \times .21 \frac{\text{moles } O_2}{\text{total moles}} =$$

0.0072 lb moles O_2/lb BDA

$$\text{moles } CO_2 = \frac{1 \text{ lb BDA}}{29 \text{ lb/lb-mole}} \times 3 \times 10^{-4} \frac{\text{moles } CO_2}{\text{total moles}} =$$

$$1.03 \times 10^{-5} \text{ lb moles } CO_2/\text{lb BDA}$$

2.2 Bowen Ash System (Units 3 or 4)

Estimates of the ash and water flow rates were calculated for the ash sluicing simulations. Also required were the result of the ash leaching studies which measured the reactivity of the fly ash. These calculations are presented below.

2.2.1 Fly Ash

Precipitator Inlet - 3.0 gr/scf

Precipitator Outlet - 0.025 gr/scf

Flue Gas - 3.0 x 10^6 ACFM @ 300°F, 1atm

$$\text{Fly Ash} = \frac{(3.0-0.025)\text{gr}}{\text{scf}} \times \frac{3.0 \times 10^6 \text{ acf}}{\text{min}} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{492 \text{ R}}{760 \text{ R}}$$

$$\times \frac{\text{lb}}{7000 \text{ gr}} = 49{,}520 \text{ lb/hr}$$

$$\text{Total Ash} = \frac{890{,}000 \text{ kW-hr}}{\text{hr}} \times \frac{9000 \text{ Btu}}{\text{kW-hr}} \times \frac{\text{lb coal}}{11{,}500 \text{ Btu}} \times \frac{.11 \text{ lb coal}}{\text{lb coal}}$$

$$= 76{,}620 \text{ lb/hr}$$

Bottom Ash = 76,620 - 49,520 = 27,100 lb/hr

2.2.2 Total Ash from all Units

Fly Ash = 205,620 lb/hr

Bottom Ash = 68,140 lb/hr

Total = 273,760 lb/hr

Sluice water required for 10% slurry of all ash:

$$\text{GPM} = \frac{273{,}760 \text{ lb ash}}{\text{hr}} \times \frac{\text{hr}}{60 \text{ min}} \times \frac{\text{gal}}{8.3 \text{ lb } H_2O} \times \frac{.90 \text{ lb } H_2O}{.10 \text{ lb ash}} = 4950 \text{ GPM}$$

2.2.3 Recirculating Ash System Flows

Blowdown from cooling towers @ 15.0 cycles = 1507 GPM

Water required for fly ash slurry = 3716 GPM

Water required for bottom ash slurry = 1230 GPM

Fly ash makeup = 1491 GPM

Bottom ash makeup = 0 GPM

Fly ash recycle = 3716 - 1491 = 2225 GPM

Bottom ash recycle = 1230 GPM

2.2.4 Pond Evaporation

Reference: PA-121

Enthalpy of evaporation = (73 + 7.3W) $(e_s - e_a)$
where W = average wind speed, mph
where e_s = saturation vapor pressure of H_2O, mmHg
where e_a = existing vapor pressure of H_2O, mmHg

For Atlanta from January '75 to November '75, average wind speed = 8.4 mph

$e_s = 1.102$ mmHg

$e_a = 0.944$ mmHg

$$\text{Hevap} = [73 + (7.3 \times 8.4)]\,[1.102 - .944] = .01765\ \frac{\text{lb}}{\text{ft}^2 - \text{day}}$$

Pond area = 250 acres = 1.089×10^7 ft^2

$$\text{Evaporation} = \frac{.01765\ \text{lb}\ H_2O}{\text{ft}\ \ -\ \text{day}} \times 1.089 \times 10\ \ \ \text{ft}\ \ \times \frac{\text{day}}{24\ \text{hr}} \times \frac{\text{hr}}{60\ \text{min}}$$

$$\times \frac{\text{gal}}{8.3\ \text{lb}} = 18.4\ \text{GPM} = 69.4\ \text{kg/min}$$

2.2.5 Ash Dissolution

Leaching studies results are shown below.

RESULTS OF CHEMICAL ANALYSIS FROM LEACHING OF ASH SAMPLES AT CONSTANT pH FOR PLANT BOWEN

	Prec. Ash[1] pH 6.0 (mmole/ℓ)[4]	Prec. Ash[2] pH 8.5 (mmole/ℓ)[4]	Prec. Ash[3] pH 10.4 (mmole/ℓ)[4]
Calcium	24.2	14.2	10.5
Magnesium	.23	.06	.01
Sodium	3.0	1.1	1.3
Potassium	.90	.72	.56
Sulfate	10.0	9.22	7.71

[1] Maintained pH of 6.0 by adding HCl.

[2] Maintained pH of 8.5 by adding HCl.

[3] Maintained pH of 10.4 by adding HCl.

[4] All values represent mmole/ℓ of soluble species in leachate after 14 grams of ash were leached in 186 grams of water at constant pH.

Using pH 10.4, 7% slurry

Assuming all sulfate is from $CaSO_4$:

$$\%CaSO_4 = \frac{7.71 \text{ mmole } CaSO_4}{\ell} \times .186 \text{ kg} \times \frac{136.1 \text{ mg}}{\text{mmole}} \times \frac{\text{g}}{1000 \text{ mg}} \times$$

$$\frac{1}{14\text{g ash}} \times 100 \times .9 = 1.25 \text{ wt\% } CaSO_4 \text{ dissolving before}$$

pond (90% of ash).

$$\%CaO = \frac{(10.5-7.71) \text{ mmole CaO}}{\ell} \times .186\text{kg} \times \frac{56.1\text{mg}}{\text{mmole}} \times \frac{\text{g}}{1000\text{mg}} \times$$

$$\frac{1}{14\text{g ash}} \times 100 = 0.21\% \text{ at pH } 10.4$$

$$\%CaO = \frac{(14.2-9.2) \text{ mmole CaO}}{\ell} \times .186 \text{ kg} \times \frac{56.1 \text{ mg}}{\text{mmole}} \times \frac{\text{g}}{1000 \text{ mg}} \times$$

$$\frac{1}{14\text{g ash}} \times 100 = 0.37\% \text{ at pH } 8.5$$

Avg = 0.3 wt%

This average was used since CaO dissolution is more pH dependent than $CaSO_4$ and is rapid.

3.0 PSC COMANCHE PLANT

Much of the data required to study the water use system at Comanche were supplied directly by Public Service of Colorado (PSC). Some of the information was calculated. This section presents the calculations which were required to simulate cooling tower and ash sluicing operations.

3.1 Comanche Cooling Towers

Estimates of the ambient air and composition were calculated for the cooling tower simulations. These calculations are presented below.

3.1.1 Inlet Air Composition

Average Winter Conditions = 32°F, 51% relative humidity

$$\text{Inlet Air} = 0.0036 \frac{\text{lb } H_2O}{\text{lb BDA}}$$

Bone Dry Air (BDA) = 78.98% N_2, 20.99% O_2, 0.03% CO_2

$$\text{mole fraction } H_2O = \frac{0.0036 \text{ lb } H_2O}{1 \text{ lb BDA} + 0.0036 \text{ lb } H_2O} \times \frac{29 \text{ lb air}}{\text{mole air}} \times \frac{\text{mole } H_2O}{18 \text{ lb } H_2O}$$

$$= 0.005779 \text{ lb moles } H_2O/\text{total lb moles moist air}$$

$$\text{mole fraction } N_2 = \frac{78.98 \text{ moles } N_2}{100 \text{ moles BDA}} \times \frac{100 \text{ moles BDA}}{100.6 \text{ moles moist air}}$$

$$= 0.7851 \text{ lb moles } N_2/\text{lb mole moist air}$$

$$\text{mole fraction } O_2 = \frac{20.99 \text{ moles } O_2}{100 \text{ moles BDA}} \times \frac{100 \text{ moles BDA}}{100.6 \text{ moles moist air}}$$

$$= 0.2087 \text{ lb moles } O_2/\text{lb mole moist air}$$

$$\text{mole fraction } CO_2 = \frac{0.03 \text{ moles } CO_2}{100 \text{ moles BDA}} \times \frac{100 \text{ moles BDA}}{100.6 \text{ moles moist air}}$$

$$= 2.98 \times 10^{-4} \text{ lb moles } CO_2\text{/lb mole moist air}$$

3.2 Comanche Ash System

Estimates of the ash flow rates, the pond evaporation and the ash reactivity were calculated for the ash sluicing simulations. These calculations are presented below.

3.2.1 Ash Flows

Coal Characterization (From Comanche Data)

Heating Value, Btu/lb	Percent Ash
7887	8.65
8131	8.09
8286	5.45
8223	7.42
9021	6.67
Avg. 8310 Btu/lb	7.26% ash

Fly Ash = 78%, Bottom Ash = 22% of total ash

Heat Lost in Cooling Water:

$$\frac{143{,}200 \text{ gal}}{\text{min}} \times \frac{1 \text{ Btu}}{\text{lb}^\circ\text{F}} \times 25.93^\circ\text{F} \times \frac{8.33 \text{ lb}}{\text{gal}} \times \frac{60 \text{ min}}{\text{hr}}$$

$= 1.856 \times 10^9$ Btu/hr removed in condenser with a ΔT of 25.93°F

Heat Input:

Assuming the plant is about 40% efficient

$$\text{Coal Rate} = \frac{1.856 \times 10^{9}\ \text{Btu/hr}}{0.6} \times \frac{\text{lb coal}}{8310\ \text{Btu}} = 3.722 \times 10^{5}\ \text{lb coal/hr}$$

$$= 6.20 \times 10^{3}\ \text{lb coal/min}$$

Assuming precipitator efficiency of 95%:

$$\text{Fly Ash} = \frac{6.20 \times 10^{3}\ \text{lb coal}}{\text{min}} \times \frac{7.26\ \text{lb ash}}{100\ \text{lb coal}} \times 0.78 \times 0.95$$

$$= \frac{333.7\ \text{lb fly ash}}{\text{min}}$$

$$\text{Bottom Ash} = \frac{6.20 \times 10^{3}\ \text{lb coal}}{\text{min}} \times \frac{7.26\ \text{lb ash}}{100\ \text{lb coal}} \times 0.22 = \frac{99\ \text{lb}}{\text{min}}\ \text{bottom ash}$$

3.2.2 Pond Evaporation

He (Enthalpy of evap.) = $(73 + 7.3W)(e_s - e_a)$ from (PA-121)

where W = average wind speed, mph

e_s = saturation pressure or H_2O, mmHg

e_a = existing partial pressure of H_2O, mmHg

Average Summer Conditions: 74°F, 51% humidity, wind speed = 7 mph

e_s = 15.46 mmHg

e_a = 10.95 mmHg

$$He = (73 + 7.3(7))\ (15.46 - 10.95)\ \frac{Btu}{ft^2\ day}$$

$$He = 559.69\ \frac{Btu}{ft^2\ day}$$

$$H_2O\ loss = \frac{559.69\ Btu}{ft^2\ day} \times \frac{lb}{1060\ Btu} \times 5410\ ft^2$$

$$\times \frac{453.6}{lb}\ g \times \frac{day}{24\ hr} \times \frac{hr}{3600\ sec}$$

H_2O loss = 151.1 g/sec

3.2.3 Ash Dissolution

Using pH 8.5, 7% slurry

From the leaching study, the amounts of dissolved species are:

	mmoles/kg H_2O
Ca	45.34
Mg	1.77
Na	1.07
K	0.15
SO_3	6.99

The actual salts present are not known, but for convenience in using these numbers in computer simulations, the sulfate was combined with calcium and the remaining cations were expressed as oxides:

	mmoles/kg H_2O	
$CaSO_4$	6.99	
CaO	38.35	
MgO	1.77	
Na_2O	0.61	(K combined with Na)

For a 7% slurry: $\frac{7\ g\ ash}{93\ g\ H_2O} \times \frac{1000\ g}{kg} = \frac{75.27\ g}{kg}\ \frac{ash}{H_2O}$

Converting moles to grams:

	mg/kg H_2O
$CaSO_4$	951
CaO	2151
MgO	71.3
Na_2O	37.8

On an ash basis, this yields:

	mg/g ash
$CaSO_4$	12.63
CaO	28.58
MgO	0.947
Na_2O	0.503

Based on analogy with the leaching studies of the Bowen Plant and Four Corners Plant, for a pH of 11.0 the dissolution will be less than at 8.5. An assumption of a 20% reduction in dissolution will give conservative results (i.e., slightly more dissolution than will probably occur). This gives:

	wt % in ash, dissolved
$CaSO_4$	1.01
CaO	2.287
MgO	0.077
Na_2O	0.041
Inerts	96.585

4.0 PP&L MONTOUR

Much of the data required to study the water use system at Montour were supplied directly by Pennsylvania Power and Light (PP&L). Some of the information was calculated. This section presents the calculations which were required to simulate the cooling tower and ash sluicing systems.

4.1 Montour Cooling Towers

For the cooling tower simulations estimates of the ambient air composition and temperature, and the heat load on the towers were calculated. In addition to these calculations a sample calculation estimating the ACB index is presented.

4.1.1 Montour Climatological Data

Weather data were obtained from PP&L in order to simulate typical weather conditions at the Montour plant. These data were used to calculate ambient air conditions as well as air flow rates through the tower. Averages for December 1975 and August 1976 are reported in Table 4-1.

TABLE 4-1. AVERAGES FOR DECEMBER 1975 AND AUGUST 1976

Month	Wet Bulb Temp., °F	Dry Bulb Temp., °F	Relative Humidity %
December 1975	28.5	31.8	68.6
August 1976	64.4	69.1	79.1

PP&L also supplied actual operating data from the condensers for December 1975 and August 1976. These data were used to obtain estimates for the cooling water temperatures, the range, and the approach. Average values were used and separate calculations were performed for each tower. The air flow rate was estimated using the method described in "Managing Waste Heat with the Water Cooling Tower" (DI-057). This method uses the concept of a rating factor, which takes into account the wet bulb, the range, and the approach. These results are presented in Table 4-2.

TABLE 4-2. COOLING TOWER OPERATING CONDITIONS

	Aug. '76 #1	Aug. '76 #2	Dec. '75 #1	Dec. '75 #2
Air in Dry Bulb, (°F)	70.2	70.2	31.8	31.8
Air in Wet Bulb, (°F)	64.4	64.4	28.5	28.5
Water in Temp., (°F)	111.9	109.6	94.3	99.7
Air Out Temp., (°F)	103	100	85	91
Water Out Temp., (°F)	84.2	81.3	61.8	60.7
Range (°F)	28	28	32.5	39
Approach (°F)	20	17	33	32
Air Flow (lb/hr)	90×10^6	100×10^6	105×10^5	95×10^6

It should be noted that the air flow rates remained essentially the same in December as in August. In fact, there was as much variation between towers in a given month as between months. For this reason the average of these four values was used in the simulations.

The composition of the input air was calculated on the basis of the relative humidity. It was assumed the ratio of N_2:O_2:CO_2 remained constant and that the change in the mole fraction of the water changed the mole fraction of the others. An example calculation using August 1976 data follows:

Basis: 1 lb BDA		mole fraction
N_2	.0272 moles	.7747
O_2	.0072	.2050
CO_2	1.03×10^{-5}	.0003
H_2O	7.22×10^{-4}	.0200
Total	.0351 moles	1.0000

$$\text{Moles of species} = \frac{\text{(mole fraction of BDA)}}{\text{(molecular weight of air)}}$$

$$N_2 = \left(\frac{.79}{29.0 \ \frac{\text{lb}}{\text{lb mole}}} \right) = .0272 \text{ moles/lb BDA}$$

$$O_2 = \left(\frac{.21}{29.0 \ \frac{\text{lb}}{\text{lb mole}}} \right) = .0072 \text{ moles/lb BDA}$$

$$CO_2 = \left(\frac{.0003}{29.0 \ \frac{\text{lb}}{\text{lb mole}}} \right) = 1.03 \times 10^{-5} \text{ moles/lb BDA}$$

Using the psychrometric chart we find under these conditions that there is:

$$\left(.013 \ \frac{\text{lb } H_2O}{\text{lb BDA}} \right)$$

Therefore:

$$\text{moles } H_2O = \left(\frac{.013}{18.016} \right) = 7.22 \times 10^{-4} \text{ lb moles/lb BDA}$$

4.1.2 Montour Heat Load

No direct information was sent by PP&L on the expected heat load on the cooling towers. Information was available on the inlet and outlet condenser temperatures as shown in Table 4-2. These data were input into the computer model and the heat load was calculated using an energy balance. As an independent check on these calculations, the cooling requirements were calculated from other data sent by PP&L. The results from this second method are presented in Appendix I. The following outlines the assumptions and calculations made to obtain these results.

Assume: Full load electric production

Electricity = 750 MW

= 1.79×10^8 cal/sec

(2.56×10^9 Btu/hr)

Assume: Design evaporation takes care of 95% of full load cooling

Evaporation = 430 ℓ/sec

(6800 GPM)

ΔH_{vap} = 586 cal/gm

(1054 Btu/lb)

Cooling load = Evap. x ΔH_{vap} x $(\frac{1}{.95})$

= 2.64×10^8 cal/sec

(3.77×10^9 Btu/hr)

Data from 3/13/75: Plant operating at 752 MW

Flue gas temp. = 140°C

(285°F)

Flow rate = 3.96×10^6 m^3/hr

(2.332×10^6 acfm)

Ambient temp. = 21°C

(70°F)

Heat capacity = .26 cal/gm

(.26 Btu/lb)

Density of air = 8.5×10^{-4} gm/cm^3

(0.53 lbm/ft^3)

Stack losses = (V)(p)(ΔT)(Cp)
= .29 x 10^8 cal/sec
(.42 x 10^9 Btu/hr)

Heat input = 4.817 x 10^8 cal/sec
(6.879 x 10^9 Btu/hr)

These data can be checked for consistency by taking the difference between the total heat in and the total heat out. The difference can easily be attributed to other losses if it is reasonably small.

Other losses = Input - (Electricity + Cooling Load + Stack Losses)
= 9.0 x 10^6 cal/sec
(1.2 x 10^8 Btu/hr)

This value is much less than any of the other heat losses and this confirms that the assumptions made in these calculations are reasonable.

4.1.3 Montour ACB Index

The ACB Index is used to determine the corrosive effects of cooling water in a cooling tower with the specific fill used at PP&L. This index, developed by the Asbestos Cement Pipe Manufacturers Association, is calculated from the following expression:

ACB = pH + Log (Calcium X Alkalinity)
with calcium and alkalinity expressed
as mg/ℓ of calcium carbonate

As an example, the calculations performed for cooling water at 4 cycles of concentration are presented below. The results for all the simulations performed are presented in Appendix I.

$$\mathrm{pH} = 7.87$$

$$\mathrm{Ca} = 113\ \mathrm{mg}/\ell\ (\text{as } \mathrm{Ca}^{++})$$

$$= 283\ \mathrm{mg}/\ell\ (\text{as } \mathrm{CaCO_3})$$

$$\text{Alkalinity} = 24.8\ \mathrm{mg}/\ell\ (\text{as } \mathrm{CO_3}^{=})$$

$$= 41.3\ \mathrm{mg}/\ell\ (\text{as } \mathrm{CaCO_3})$$

$$\mathrm{ACB} = 7.87 + \mathrm{Log}\ [(283)\cdot(41.3)]$$

$$= 11.94$$

4.2. Montour Ash System

For the sluicing runs estimates of the fly ash, bottom ash, pyrite, and water flows were made. Due to the amount of data made available, some of these flow rates were calculated by more than one method. Also required were calculations of the pond evaporation rate, the ash reactivity, and the calcium removal rate. All of these calculations are presented in this subsection.

4.2.1 Montour Fly Ash

Fly ash flow rates for one plant were estimated by the two methods shown below.

Method A

Assume: 99% efficiency from the electrostatic precipitator

Typical dust flow was reported as 685 lb/hr.

$$\text{Fly Ash} = \frac{\text{Dust}}{1. - E} - \text{Dust}$$

$$= \frac{685\ \mathrm{lb/hr}}{1. - .99} - 685\ \mathrm{lb/hr}$$

$$= 67815\ \mathrm{lb/hr}$$

$$= 30825\ \mathrm{kg/hr}$$

Method B

From data collected from 5/11/76 to 5/13/76

Fly Ash Sluice = 2730 GPM

Weight % Solids = 4.79

$$\text{Fly Ash} = (\text{wt. of water})\left(\frac{\%\ \text{solids}}{100-\%\ \text{solids}}\right)$$

$$= (13.6 \times 10^5\ \text{lb/hr})\ \frac{4.79}{100 - 4.79}$$

$$= 68400\ \text{lb/hr}$$

$$= 31100\ \text{kg/hr}$$

The second value was used in the simulations, because it was larger and represented a worse case. The first value served as a very good check on the reliability of the second calculation.

4.2.2 Montour Bottom Ash and Mill Rejects

Data were available on the amount of bottom ash and mill rejects that were sluiced from 5-11-76 to 5-13-76. Sluicing of these solids is not done on a continuous basis, but is run intermittently. From these data the solid flow rates were calculated (normalized to a continuous basis).

Bottom Ash Sluice = 1680 GPM = 8.37×10^5 lb/hr (using density of 8.3 lb/gal)

Weight % Solids = 4.46

$$\text{Bottom Ash} = (8.37 \times 10^5\ \text{lb/hr})\ \left(\frac{4.46}{100-4.46}\right)$$

$$= 39100\ \text{lb/hr}$$

$$= 17760\ \text{kg/hr}$$

Mill Reject Sluice = 1550 GPM = 7.72×10^5 lb/hr

Weight % Solids = 0.54

$$\text{Mill Rejects} = (7.72 \times 10^5 \text{ lb/hr}) \left(\frac{0.54}{100 - 0.54}\right)$$

$$= 4200 \text{ lb/hr}$$

$$= 1900 \text{ kg/hr}$$

For purposes of the simulation the bottom ash and mill rejects sluicing operations were combined. Since the mill rejects are actually sluiced at one-tenth the percent solids used for the bottom ash the total mass flow of the mill rejects was increased by a factor of ten. This has the effect of requiring the same amount of water to sluice the mill rejects as is actually needed and allowing the mill reject sluicing operation to be combined with the bottom ash sluicing for purposes of simulation.

$$\text{Bottom Ash + Mill Rejects} = 81{,}100 \text{ lb/hr}$$

$$36{,}760 \text{ kg/hr}$$

The Montour station has reported that their cooling towers operate on the average near 2 cycles. The blowdown from the cooling towers operating at 2 cycles is less than that which was required to sluice all the ash at 5% solids. In order to have the ash sluiced at 5% solids with the blowdown from the cooling towers operating at 2 cycles, the amount of bottom ash was reduced from 36,760 kg/hr to 33,500 kg/hr. This has the effect of increasing the ratio of reactive fly ash to non-reactive bottom ash. This is a conservative assumption when applied to the recycle alternatives presented in this report, in that it increases the concentration of the ionic species in the ash pond, and the scaling potential.

4.2.3 Montour Pond Evaporation

The evaporation rate was estimated using a technique presented in PA-121. Weather conditions were those found in August 1976.

$$E = [(73 + 7.3\ W)\ (e_s - e_a)]/\Delta H_{vap}$$

w = wind speed, mph

e_s = saturation vapor pressure of H_2O, in. Hg

e_a = existing vapor pressure of H_2O, in. Hg

ΔH_{vap} = enthalpy of evaporation, Btu/lb

E = evaporation flux, lb/ft^2 - day

$E = [\{73 + 7.3(5.3)\}](.712 - .618)/1050$

$= .011\ lb/ft^2$ - day

The area of the ash pond has been estimated to be $2.4 \times 10^6\ ft^2$.

$$\text{Evaporation rate} = (2.4 \times 10^6)\ (.0100)$$
$$= 2.4 \times 10^4\ lb/day$$
$$= 20.1\ gpm$$
$$= 1.26\ \ell/sec$$

An evaporation rate of .63 ℓ/sec (10 gpm) was used in the simulations, since half the pond was used by each unit.

4.2.4 Montour Calcium Removal Rate

Some of the ash sluicing results presented in Appendix I employ sodium carbonate softening in order to reduce calcium levels and prevent $CaSO_4$ scale formation in the sluice line. A slipstream is taken from the recycle line where the calcium concentration is lowered to 50 mg/ℓ. The equations used to determine the calcium removal rate and the size of the slipstream are presented below.

$$C' = \frac{RS'}{RS} C \qquad (1)$$

$$Ca' = \frac{C' - CI}{(MW)(H_2O)_r} \qquad (2)$$

$$Ca' = Ca''x + Ca(1-x) \qquad (3)$$

$$CR = x\ (Ca - Ca'')(H_2O)_r/(MW) \qquad (4)$$

$$Ca = (CI - CR)(MW)/(H_2O)_s \qquad (5)$$

where:

Ca = calcium in the pond with softening (mg/ℓ)
Ca' = calcium in the recycle after softening (mg/ℓ)
Ca'' = calcium in the slipstream after softening (mg/ℓ)
C = calcium in the slurry before softening (mole/sec)
C' = calcium in the slurry after softening (mole/sec)
CR = calcium removal rate (moles/sec)
CI = calcium input from the ash and the make-up water (moles/sec)
RS = relative saturation of $CaSO_4$ in the slurry stream before softening
RS' = relative saturation of $CaSO_4$ in the slurry stream after softening
$(H_2O)_r$ = water in the recycle stream (ℓ/sec)
$(H_2O)_s$ = water in the sludge (ℓ/sec)
MW = atomic weight of Ca (mg/mole)
x = fraction of the recycle used for slipstream treatment

Equation (1) assumes that the activity coefficients of Ca^{++} and $SO_4^{=}$ remain constant and gives an estimate of the desired calcium level in the slurry stream in order to eliminate $CaSO_4$ scale. Equation (2) calculates the required calcium level in the recycle to reach C' in the slurry stream. Equation (3) determines the minimum slipstream that must be treated to obtain a concentration of Ca' in the recycle. Equation (4) calculates the calcium removal rate for a given sized slipstream. Equation (5) is an overall mass balance. In the following, these equations are used to determine the softening required for Alternative 1 using 8 cycle cooling tower blowdown as makeup water.

$$C' = \left(\frac{0.95}{3.147}\right) 6.749 \tag{1}$$

$$C' = 2.037 \text{ moles/sec}$$

$$Ca' = \frac{2.037 - .7533}{(4.01x10^4)(143)} \qquad (2)$$

$$Ca' = 389 \text{ mg}/\ell$$

The last three equations were combined to form Equation (6) and solved for the calcium removal rate (CR), the fraction of the recycle that must be softened (x), and the concentration of calcium in the pond (Ca).

$$Ca = \frac{(CI \cdot MW)+(Ca' \cdot (H_2O)_r)}{(H_2O)_s(1 + (H_2O_r/(H_2O_s)} \qquad (6)$$

$$Ca = \frac{(.753 \cdot 4.01x10^4) + (389 \cdot 143)}{(143)\ (1 + (143/16.8)\ )}$$

$$Ca = 537 \text{ mg}/\ell$$

$$CR = (Ca - Ca')(H_2O)_r/MW \qquad (3 + 4)$$

$$CR = (537 - 389)(143)/4.01x10^4$$

$$CR = 0.528 \text{ moles/sec}$$

$$x = \left(\frac{Ca - Ca'}{Ca - Ca''}\right)$$

$$x = \left(\frac{537 - 389}{537 - 50}\right)$$

$$x = .304$$

4.2.5 Montour Ash Dissolution

In order to simulate the ash sluicing system at Montour it was necessary to obtain information on the different soluble species in the ash. In order to make an estimate of the amount of calcium, magnesium, sodium, and sulfate that is leached from this ash, batch dissolution studies were carried out.

4.2.5.1 Procedure

Four experiments were performed using the Montour ash, two at pH 6 and two at pH 8.1. Under each pH condition the weight percent solids was varied. In each case, 200 grams of deionized water were used with either 10 or 20 grams of ash. Under these conditions, weight percent solids of 4.8% and 9.1% were attained. In order to maintain pH 6, HCl was added and the amount was recorded as a function of time. No acid was necessary to attain pH 8.1, but the pH was recorded as a function of time.

Figure 4-1 is a plot of HCl added versus time for both the 4.8 percent and the 9.1 percent slurries. From this graph it can be seen that more than half the alkalinity, 53 percent and 64 percent, respectively, is leached from the ash in the first fifteen minutes. Figure 4-2 is a plot of pH versus time for both slurries when the pH was allowed to float (pH = 8.1). Within the first fifteen minutes almost all of the changes in pH had occurred. This evidence suggests that most of the alkalinity in the ash, in a five to ten percent slurry, should be leached out in the first fifteen minutes.

4.2.5.2 Results

The liquors from the four slurries were analyzed for calcium, magnesium, sulfate, and sodium. These analyses gave the concentration of each species which was then used to obtain the reactive amount of each on a weight percent basis. Table 4-3 lists the results obtained under each operating condition. The values are reported as weight percent of the dry ash.

TABLE 4-3. ASH LEACHING RESULTS

	5% Slurry		10% Slurry		
	pH = 6 (wt.%)	pH = 8.1 (wt.%)	pH = 6 (wt.%)	pH = 8.1 (wt.%)	Average (wt.%)
Calcium (as Ca)	0.329	0.287	0.317	0.273	0.302
Magnesium (as Mg)	0.019	0.017	0.018	0.016	0.018
Sodium + Potassium (as Na)	0.041	0.041	0.040	0.038	0.040
Sulfate (as SO_4)	0.768	0.797	0.759	0.778	0.776

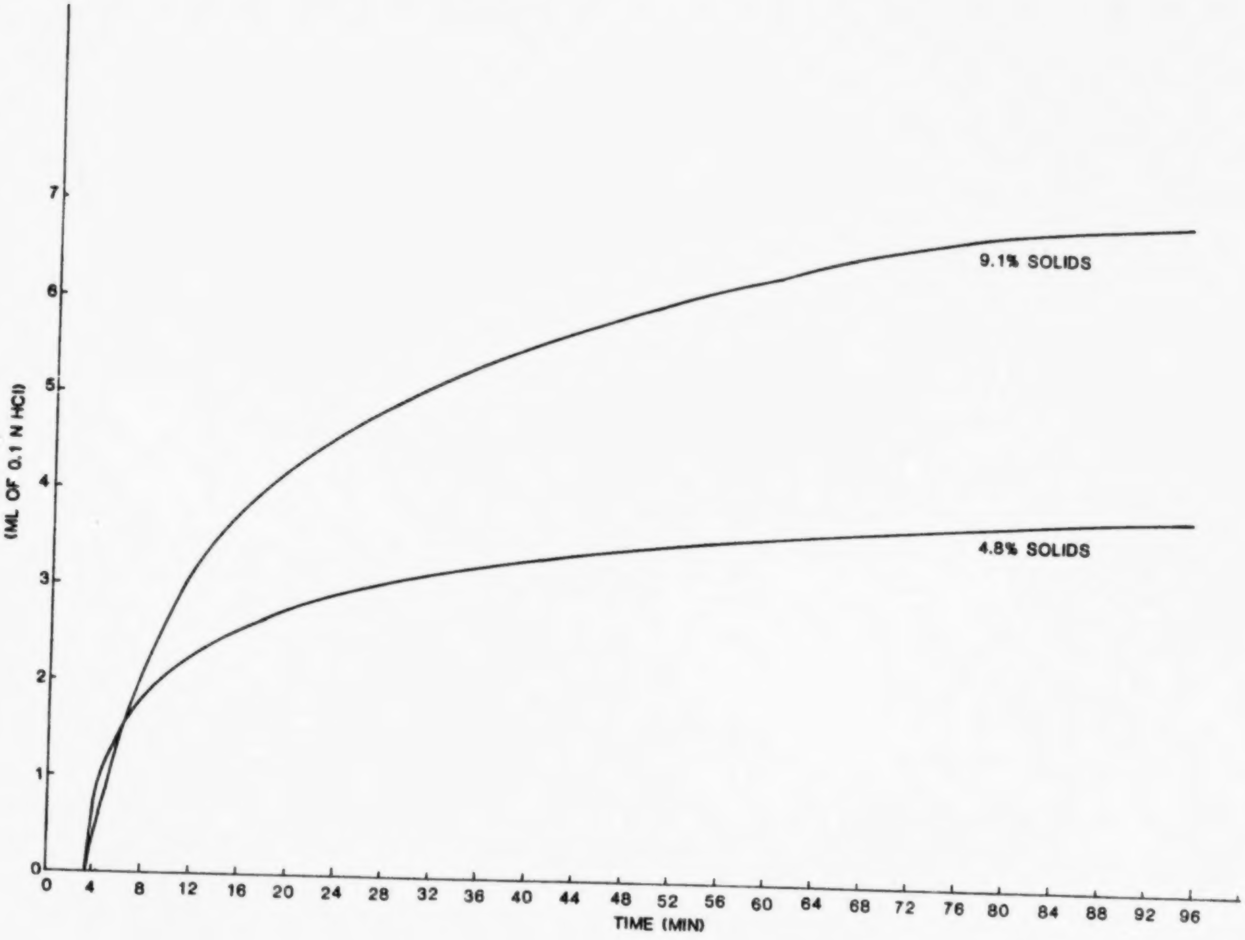
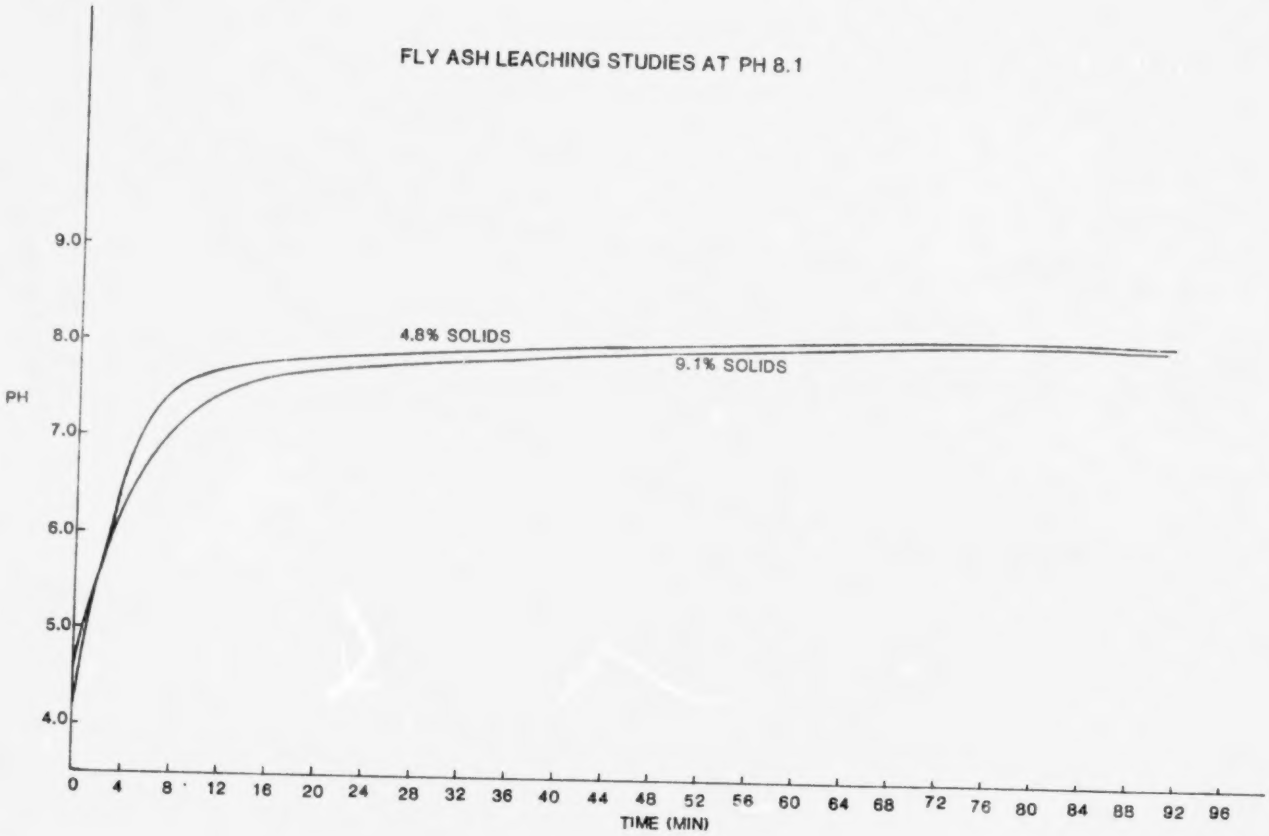


Figure 4-1. Fly ash leaching studies at pH 6.0.

02-1165-1



02-1166-1

Figure 4-2. Fly ash leaching studies at pH 8.1.

This study was performed under idealized conditions, substantially different from those which the ash would see in actual operation. These results should represent the worst case, since deionized water was used. The higher ionic strength of the slurry water in an actual plant would probably leach less from the ash. In order to simulate actual conditions, a bench-scale ash sluicing experiment has been performed using more representative water. The results of this experiment are presented in Appendix D.

The data in Table 4-3 are only estimates of the reactivity of the ash used at Montour. The average values in column five were used to generate the inputs required for the ash sluicing simulations. The required calculations are presented below.

Convert from wt. % to mmoles/gm:

$$Ca = \frac{(.302)}{100\ (4.01 \times 10^{-2})} = 0.0753 \text{ mmoles/gm}$$

$$Mg = \frac{(.018)}{100\ (2.43 \times 10^{-2})} = 0.0074 \text{ mmoles/gm}$$

$$Na = \frac{(.040)}{100\ (2.30 \times 10^{-2})} = 0.0174 \text{ mmoles/gm}$$

$$SO_4 = \frac{(.776)}{100\ (9.60 \times 10^{-2})} = 0.0808 \text{ mmoles/gm}$$

Combine anions and cations to account for all species and convert to wt. %:

$CaSO_4$ = 0.0753 mmoles/gm = 1.025 wt. %

$MgSO_4$ = 0.0055 mmoles/gm = 0.066 wt. %

MgO = 0.0019 mmoles/gm = 0.008 wt. %

NaO = 0.0174 moles/gm = 0.054 wt. %

The rest of the ash was assumed to be inert and equal to 98.847 wt. %.

5.0 MPC COLSTRIP

Much of the data required to study the water use system at Colstrip were supplied directly by Montana Power Company (MPC). Some of the information was calculated. This section presents the methods used to calculate the data required to simulate the cooling tower and SO_2-particulate scrubbing systems.

5.1 Colstrip Cooling Towers

Estimates of the ambient air composition and temperature were calculated to simulate the cooling towers at Colstrip. These calculations are presented in this subsection.

5.1.1 Colstrip Climatological Data

Weather data was obtained for Billings, Montana, for January-October 1976. These data were used to calculate ambient air conditions. Averages for summer and winter operation are shown in Table 5-1.

TABLE 5-1. AVERAGE CLIMATOLOGICAL DATA FOR BILLINGS, MONTANA

Month	Wet Bulb Temp., F.	Dry Bulb Temp., F.	Relative Humidity, %
Summer (June, July, Aug.)	55	69	40
Winter (January, February)	24	30	42

The composition of the input air was calculated on the basis of the relative humidity. It was assumed that the ratio of N_2 to O_2 to CO_2 remained constant and the change in the mole fraction of the water changed the mole fraction of the others. An example calculation for winter operation follows:

Basis: 1 lb. Bone Dry Air (BDA)

	Moles	Mole %
N_2	.0272	78.8
O_2	.0072	20.9
CO_2	1.03×10^{-5}	.03
H_2O	7.77×10^{-5}	.23
Total	.0345	100.

$$\text{Moles of species} = \frac{\text{mole fraction of BDA}}{\text{molecular weight of air}}$$

$$N_2 = \left(\frac{.79}{29.0 \frac{\text{lb}}{\text{lb mole}}}\right) = .0272 \text{ moles/lb BDA}$$

$$O_2 = \left(\frac{.21}{29.0 \frac{\text{lb}}{\text{lb mole}}}\right) = .0072 \text{ moles/lb BDA}$$

$$CO_2 = \left(\frac{.0003}{29.0 \frac{\text{lb}}{\text{lb mole}}}\right) = 1.03 \times 10^{-5} \text{ moles/lb BDA}$$

Using the psychrometric chart for a wet bulb temperature of 24°F and a dry bulb temperature of 30°F, the water content is:

.0014 lb H_2O/lb BDA or .0023 lb moles H_2O/lb mole BDA

Therefore:

$$\text{moles } H_2O = \frac{.0014}{18.016} = 7.77 \times 10^{-5} \text{ lb moles } H_2O\text{/lb BDA}$$

5.2 Colstrip Scrubbing System

Estimates of the flue gas composition and the ash reactivity were calculated to simulate the scrubbing system at Colstrip. The methods used to calculate these data and perform the sample consistency check are presented in this subsection.

5.2.1 Colstrip Flue Gas Composition

The average coal analysis reported by MPC was used to determine the flue gas composition entering the scrubbers. The particulate loading supplied by MPC of 725 lb/min ash (design value) was used with the calculated flue gas composition as input to the model. The coal used and the resulting flue gas compositions are shown in Table 5-2.

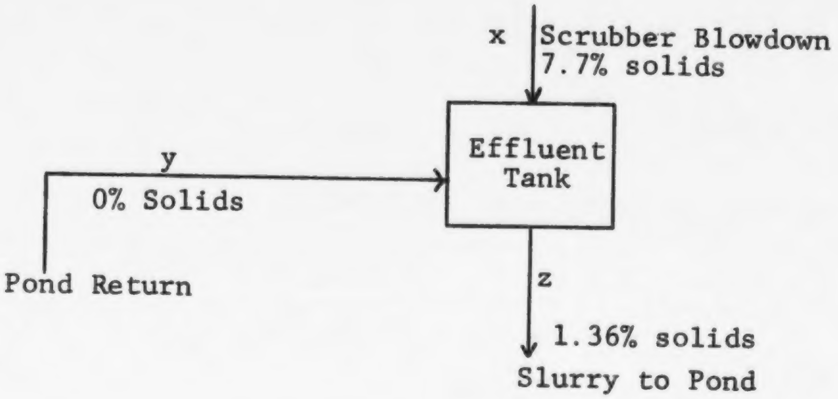
TABLE 5-2. COAL AND FLUE GAS COMPOSITIONS

	Coal (wt. fraction)		Flue Gas (mole %)
C	.579	CO_2	14.1
H	.038	H_2O	9.5
O	.119	O_2	3.5
N	.0086	N_2	72.8
S	.0085	SO_2	.08
Moisture	.15	Flow, acfm (both units)	2.75×10^6
Ash	.097		

No chloride content of either the coal or flue gas was reported, but the scrubbing simulations predicted chloride levels well, indicating that very small amounts, if any, of chloride enter the scrubbing system by the flue gas.

A firing rate of 400 tons/hr (both units) with 21% excess air fired was used to determine the gas flow. The flue gas temperature of 291°F was supplied by MPC.

5.2.2 Colstrip Effluent Tank Sample Consistency



Let x = flow of scrubber blowdown,
y = flow of pond return, and
z = flow of slurry to pond.

By material balance

$$x + y = z$$

By solids balance (assuming negligible solid formation and/or dissolution):

$$.077x = .0136z$$

or

$$z = \frac{.077}{.0136}x = 5.662x$$

$$y = z - x = 4.662x$$

Now a species balance can be written as follows with C_{ij} being the concentration of species i in stream j:

$$C_{ix}(x) + C_{iy}(y) = C_{iz}(z)$$

substituting for z and y,

$$C_{ix}(x) + C_{iy}(4.622x) = C_{iz}(5.662x)$$

dividing by x,

$$C_{ix} + 4.662C_{iy} = 5.662C_{iz}$$

Since flows have been eliminated, the sample consistency may be checked as follows:

$$\Sigma\text{In} = C_{ix} + 4.662C_{iy}$$

$$\Sigma\text{Out} = 5.662C_{iz}$$

$$\%\ \text{Error} = \frac{\Sigma\text{In} - \Sigma\text{Out}}{(\Sigma\text{In} + \Sigma\text{Out})/2}$$

For each species, the concentrations in the three streams are known, and the % error may be calculated. The results of this calculation are presented in Appendix J.

5.2.3 Colstrip Ash Dissolution

Three experiments were performed to characterize the ash from Colstrip coal. The actual samples were taken from MPC's J.E. Corette plant in Billings, Montana. This plant burns the same coal as Colstrip. The reason this sample was used was that a dry ash sample at Colstrip was not obtainable.

The three experiments involved slurrying 20 grams of ash in 180 mℓ of deionized water with the pH held constant by HCl addition. pH values of 4.0, 6.0, and 8.0 were used to characterize the alkalinity leached from the ash as a function of pH. After all the alkalinity was leached (no more acid addition required) a sample of the leachate was analyzed for calcium, magnesium, sulfate, and sodium. No appreciable sodium was found in the Corette ash.

Table 5-3 presents the results of the three experiments performed for the MPC ash. The values for concentration in the final leachate were used to calculate the leachable species as a fraction of the dry ash.

TABLE 5-3. ASH LEACHING RESULTS

Species	pH=4 (wt%)	pH=6 (wt%)	pH=8 (wt%)
$CaSO_4$	0.78	0.85	0.81
CaO	6.8	4.8	4.1
MgO	1.1	.35	.10
Na_2O	--	--	--

These results show that calcium dissolution from the ash is strongly dependent on pH, varying from 6.8% at pH4 to 4.1% at pH8. Magnesium dissolution is considerably smaller but is still very pH dependent. The amount of sulfate leached from the ash (assumed as $CaSO_4$) does not vary significantly with pH but remains at about .8%.

Since this ash did not actually come from the Colstrip plant, these results were not used in the simulations. Instead, the ash composition was calculated based on the overall alkalinity required and the design lime addition rate. These calculated values are shown in Table 5-4 along with the fly ash analysis provided by MPC.

TABLE 5-4. COMPARISON OF CALCULATED, SAMPLE, AND MPC FLY ASH REACTIVITY

Species	Sample (pH=4.0) (wt%)	Calculated (wt%)	MPC Data (wt%)
$CaSO_4$	0.78	--	--
CaO	6.8	17.9	21.9
MgO	1.1	1.3	4.95
Na_2O	--	0.035	0.31

The calculated values are much closer to the MPC data than the sample values. The sample values possibly vary due to the ash being taken from another plant. The scrubber environment may also cause increased leaching of the ash species due to the acidic species sorbed. If the sample value for calcium is used for the ash, then the lime addition rate to the system would be 4000 kg/hr (8800 lb/hr) as opposed to the design rate of 760 kg/hr (1670 lb/hr).

APPENDIX L

ASH CHARACTERIZATION FOR FOUR CORNERS, BOWEN, AND COMANCHE FLY ASHES

ABSTRACT

A study under EPA Contract No. 68-02-1319 was made to perform a preliminary characterization of ash dissolution and CO_2 mass transfer occurring in fly ash sluicing operations of coal-fired steam-electric generating stations. This task was performed in support for EPA Contract No. 68-03-2339, Water Recycle/Reuse Alternatives in Coal-Fired Steam-Electric Power Plants. The three plants studied in the Water Recycle/Reuse programs are also the sites of the ashes used in this study. These plants are: (1) Public Service of Colorado, Comanche Plant; (2) Arizona Public Service, Four Corners Plant; and (3) Georgia Power Company, Plant Bowen.

Three major types of tests were performed: (1) carbon dioxide sorption, (2) bench-scale closed-loop sluicing, and (3) fly ash leaching and batch dissolution. The carbon dioxide sorption tests were made so that an estimate of the amount of CO_2 absorbed from the atmosphere in a settling pond of an ash sluicing system could be made. Experiments with both agitated and stagnant systems were made at pH values of 9.0 and 11.0.

The bench-scale closed-loop sluicing tests were made to characterize the dissolution of fly ashes as a function of liquor composition. The variables considered include makeup water composition, sluice tank residence time, carbonate sorption in the settling pond, sluice-line residence time and ash composition.

The ash leaching tests were performed to determine the total alkalinity available in each ash and the rate at which it dissolves as a function of liquor pH. Batch dissolution experiments were made to test the effect of liquor composition on the ash dissolution characteristics. The results are qualitatively compared to the results of the closed-loop sluicing tests.

1.0 INTRODUCTION

This project was performed under EPA Contract No. 68-02-1319 to gather information concerning the chemical characteristics of ash sluicing systems in support for EPA Contract No. 68-03-2339, Water Recycle/Reuse Alternatives in Coal-Fired Steam-Electric Power Plants. In this section, background information for the project is first presented followed by a summary of the program.

1.1 Background

To evaluate the ash sluicing systems studied in the water recycle/reuse project, dissolution characteristics of the ash and the degree of carbon dioxide mass transfer between the atmosphere and process liquor must be known.

This task was performed to provide data concerning CO_2 mass transfer between process liquors and the atmosphere, and the dissolution characteristics of the ashes from the plants under study in the water recycle/reuse program. This information is vital in predicting scaling tendencies throughout the ash sluicing systems for $CaCO_3$, $Mg(OH)_2$, and $CaSO_4 \cdot 2H_2O$. The following section will present a description of the tests performed and a brief summary of the results.

1.2 Summary

Three major types of experiments were performed using the ashes from: 1) Public Service of Colorado, Comanche Station; 2) Arizona Public Service, Four Corners Station; and 3) Georgia Power, Plant Bowen. The three types of tests are: 1) carbon dioxide sorption, 2) closed-loop sluicing, and 3) leaching and batch dissolution.

1.2.1 Carbon Dioxide Sorption

The CO_2 sorption experiments were performed using liquors with pH values of 9.0 and 11.0 in both stagnant and agitated vessels. Carbonate concentrations were measured at various depths in the stagnant runs and at one location for the agitated runs as a function of time.

Carbonate concentrations in the pH 11 stagnant runs were rougly three times as great as in the pH 9 stagnant runs, indicating a significant enhancement of CO_2 sorption at higher pH values. Higher sorption rates were also obtained by installing an instrument fan to blow air across the surface of the container to prevent the formation of a CO_2-poor layer of air at the air-water interface.

Rapid aqueous dispersion of CO_2 was observed in the stagnant experiments as evidenced by the uniformity of carbonate concentrations at various depth levels. The results of the CO_2 sorption tests are discussed in greater detail in Section 2.0.

1.2.2 Closed-Loop Sluicing

Bench-scale closed-loop sluicing tests were performed to characterize the dissolution of fly ashes as a function of liquor composition. The bench-scale model included a mix tank where ash and makeup water were added, a sluice line, and a settling pond.

The closed-loop tests for ashes from all three plants showed high calcium carbonate relative saturations, indicative of a potential scaling problem. All three sets of runs indicated low magnesium concentrations although supersaturation of $Mg(OH)_2$ was noted in the Comanche and Bowen tests due to high hydroxide concentrations.

Both CaO and $CaSO_4$ were major species dissolving from the ashes from Comanche and Bowen. Gypsum ($CaSO_4 \cdot 2H_2O$) supersaturation was observed in both cases, probably resulting from rapid CaO dissolution to provide high calcium levels and dissolution of calcium sulfate (in a form other than gypsum) to provide both calcium and sulfate ions. Both gypsum and magnesium hydroxide were below saturation levels for all of the runs using Four Corners fly ash.

Another observation was that lower pH values in the system (obtained by bubbling CO_2 into the pond liquor) tend to enhance CaO dissolution more than $CaSO_4$ dissolution. Detailed discussions of the results and graphs prepared to show the dissolution characteristics of each ash are presented in Section 3.0.

1.2.3 Leaching and Batch Dissolution

Leaching tests were performed to determine the available alkalinity and the concentrations of chemical species dissolved from the ashes at various pH values. Batch dissolution experiments were conducted to ascertain the effects of liquor composition on ash dissolution by means of a simple laboratory test. The pH of the liquor in the leaching studies was maintained by adding a measured amount of acid, whereas in the batch dissolution tests, the pH was not controlled.

The leaching tests indicated that the major source of alkalinity in all three cases is CaO. Calcium and sulfate were the major species leached from the Comanche and Bowen ashes. Sulfate was leached from the Four Corners ash but at a much smaller level than the other ashes. Also, as in the closed-loop sluicing tests, lower pH values enhanced the dissolution of calcium more than sulfate.

The batch dissolution characterizations confirmed the results of the leaching tests in that calcium is the major species dissolving. The calcium dissolution produces high pH values (10-12) and calcium carbonate supersaturation. For the Comanche ash, calcium sulfate precipitation was evidenced by a decrease in sulfate concentration, presumably by gypsum formation, although gypsum relative saturations were less than one.

For the Bowen ash, calcium and sulfate were the major dissolving species although lower concentrations were encountered than in the closed-loop sluicing experiments. Liquor pH values as compared to those measured in the closed-loop runs were similar for the Comanche ash, slightly lower for the Bowen ash, and slightly higher for the Four Corners ash. A more detailed discussion of the leaching and batch dissolution results is presented in Section 4.0.

2.0 CARBON DIOXIDE SORPTION TESTS

The purpose of this subtask was to determine the degree of carbon dioxide mass transfer from the atmosphere into an aqueous medium. This information is necessary to determine the effect of carbon dioxide transfer upon the chemical equilibrium of the sluice water of an ash sluicing facility. Carbon dioxide mass transfer rates are necessary in the determination of the pH of the settling pond of an ash sluicing facility.

2.1 Technical Approach

Carbon dioxide sorption characteristics of aqueous mediums at pH levels of 9 and 11 were determined. The effects of depth and agitation of the system were also examined. Both agitated and stagnant systems were used.

The tests were performed in 60.8ℓ (16 gal) linear polyethylene containers. Rubber septums were mounted in the walls of the test containers so that samples could be taken directly by a syringe. The samples were then injected into a nondispersive infrared CO_2 analyzer. The sampling ports of the stagnant system were positioned 5.1, 20.3, 40.6, and 61.0 cm (2, 8, 16, and 24 inches) below the surface of the test liquor. A peristaltic pump was used to mix the test medium of the agitated system by transferring liquor from the top to the bottom of the test container at a rate of 250 ml/min. Due to the consistency of the test medium, the agitated system necessitated only one sampling port which was 15.2 cm (6 inches) below the surface. Figure 2-1 is a depiction of the test containers indicating the positions of the sample ports for both the stagnant and agitated systems.

2.2 Experimental

2.2.1 pH = 11, Nonbuffered Test Medium

The initial experiment was performed to measure the carbon dioxide sorption rate into an aqueous medium of deionized water with the pH adjusted to 11 by sodium hydroxide. The test solutions were adjusted to this pH at the start of the run, and the pH of the agitated system was periodically readjusted to this value. The pH of the stagnant system was not readjusted during the experiment so as not to disturb the system. Samples were drawn 17, 48, and 89 hours into the run, and the results appear in Table 2-1.

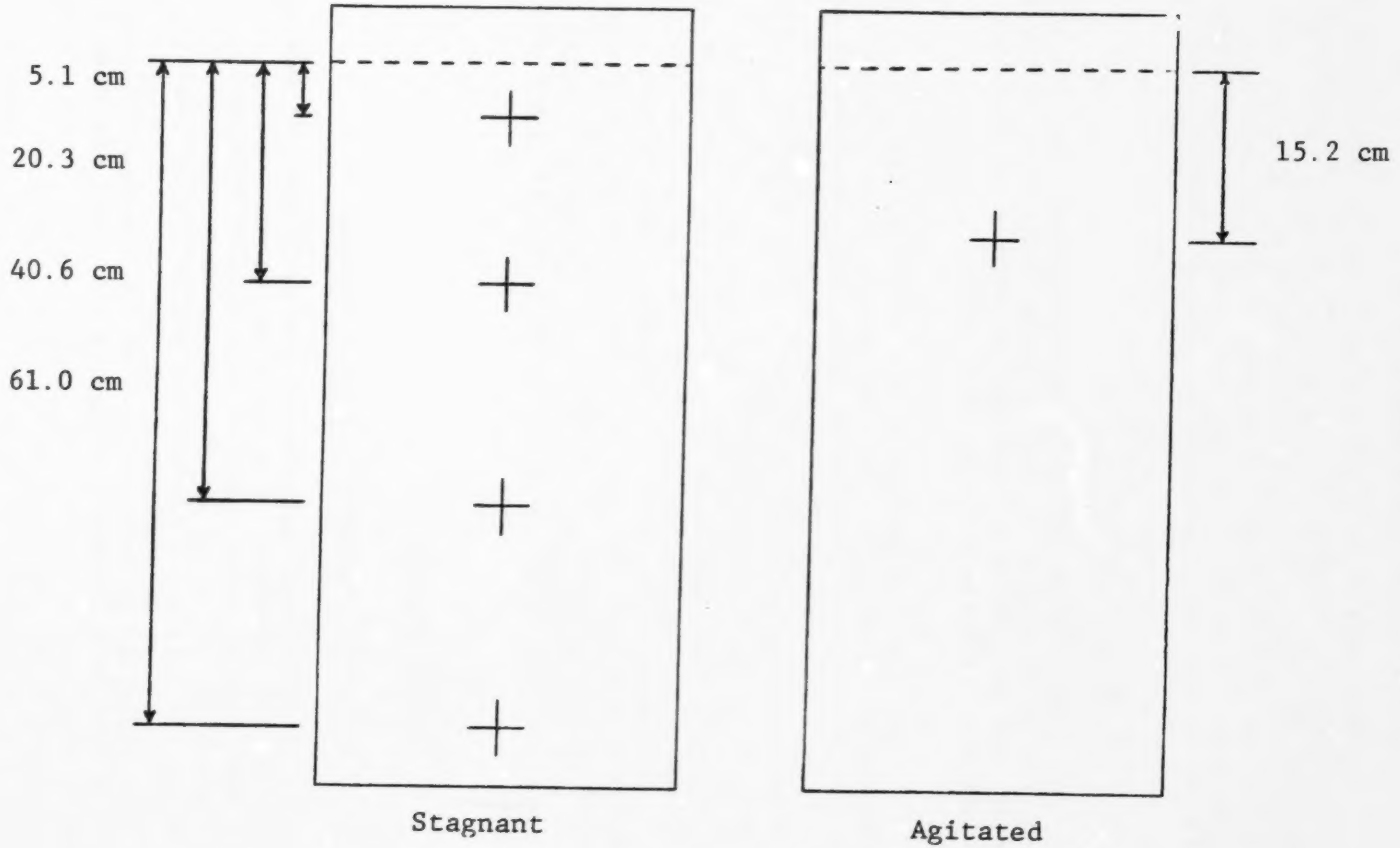


Figure 2-1. Test containers.

TABLE 2-1. CO_2 SORPTION - NONBUFFERED pH = 11

Time	Initial	17 Hours	48 Hours	89 Hours
STAGNANT SYSTEM				
5.1 cm below Surface	<.5 mg/1 <.001 mg/1/cm^2	3.7 mg/1 .004 mg/1/cm^2 .0002 mg/1/cm^2/hr	12.6 mg/1 .014 mg/1/cm^2 .0003 mg/1/cm^2/hr	20.1 mg/1 .022 mg/1/cm^2 .0002 mg/1/cm^2/hr
20.3 cm below Surface	<.5 mg/1 <.001 mg/1/cm^2	2.8 mg/1 .003 mg/1/cm^2 .0002 mg/1/cm^2/hr	10.4 mg/1 .011 mg/1/cm^2 .0002 mg/1/cm^2/hr	19.8 mg/1 .022 mg/1/cm^2 .0002 mg/1/cm^2/hr
40.6 cm below Surface	<.5 mg/1 <.001 mg/1/cm	2.4 mg/1 .003 mg/1/cm^2 .0002 mg/1/cm^2/hr	11.6 mg/1 .013 mg/1/cm^2 .0003 mg/1/cm^2/hr	19.7 mg/1 .022 mg/1/cm^2 .0002 mg/1/cm^2/hr
61.0 cm below Surface	<.5 mg/1 <.001 mg/1/cm^2	2.6 mg/1 .003 mg/1/cm^2 .0002 mg/1/cm^2/hr	11.1 mg/1 .012 mg/1/cm^2 .0002 mg/1/cm^2/hr	19.3 mg/1 .021 mg/1/cm^2 .0002 mg/1/cm^2/hr
AGITATED SYSTEM	<.5 mg/1 <.001 mg/1/cm^2	5.3 mg/1 .006 mg/1/cm^2 .0004 mg/1/cm^2/hr	15.6 mg/1 .017 mg/1/cm^2/hr .0004 mg/1/cm^2/hr	37.0 mg/1 .041 mg/1/cm^2 .0005 mg/1/cm^2/hr

Volume of the test container was 60.83 liters.
Surface area of the test container was 907.92 cm^2.

2.2.2 pH = 11, Buffered Test Medium

This experiment was also performed at pH 11, but the pH was maintained by buffering the test medium with KH_2PO_4, NaOH, and HCl. Also small instrumentation fans were positioned to blow air across the surface of the test liquor. The purpose of these fans was to prevent the creation of a diffusion layer in the air just above the liquor. If the air above the test medium is stagnant, the air in contact with the liquor will have a reduced CO_2 concentration due to the sorption of CO_2 by the water. A diffusion layer will then be formed in the air above the test medium whereby this low CO_2 concentration air will be replenished by the air of higher CO_2 concentration just above it. Table 2-2 contains the data collected in this experiment. Samples were taken 24, 48, and 70 hours into the run.

2.2.3 pH = 9, Buffered Test Medium

A pH of 9 was maintained in this run by using sodium tetraborate decahydrate as a buffer. The instrumentation fans were again positioned to prevent the depletion of CO_2 above the test liquor. Samples were withdrawn 20, 44, and 50 hours into the run. The data collected in this experiment appears in Table 2-3.

2.3 Data

Tables 2-1, 2-2, and 2-3 contain the data collected during the experiments. The concentration of carbon dioxide appears first, then the concentration as a function of surface area, and last, the sorption rate of carbon dioxide expressed as a concentration flux.

2.4 Conclusions

The results of the nonbuffered pH 11 run indicated that the rate of carbon dioxide sorption is higher in an agitated system than in a stagnant system. This would be anticipated due to more water of lower concentration with respect to CO_2 being made available at the surface for reaction. The carbon dioxide concentrations at all the sampling points of the stagnant system were similar with only a small increase in CO_2 concentrations close to the surface of the test solution. A more concentrated layer of CO_2 was expected near the surface. However, dissolved carbon dioxide diffuses rapidly in aqueous media. Evidence of fast diffusion of dissolved carbon dioxide was apparent in each experimental run from the uniformity of concentrations in the stagnant systems.

TABLE 2-2. CO_2 SORPTION - BUFFERED pH = 11

Time	Initial	24 Hours	48 Hours	70 Hours
STAGNANT SYSTEM				
5.1 cm below Surface	<.5 mg/l <.001 mg/l/cm^2	6.7 mg/l .007 mg/l/cm^2 .0003 mg/l/cm^2/hr	15.8 mg/l .017 mg/l/cm^2 .0004 mg/l/cm^2/hr	24.5 mg/l .027 mg/l/cm^2 .0004 mg/l/cm^2/hr
20.3 cm below Surface	<.5 mg/l <.001 mg/l/cm^2	6.7 mg/l .007 mg/l/cm^2 .0003 mg/l/cm^2/hr	15.1 mg/l .017 mg/l/cm^2 .0004 mg/l/cm^2/hr	24.0 mg/l .026 mg/l/cm^2 .0004 mg/l/cm^2/hr
40.6 cm below Surface	<.5 mg/l <.001 mg/l/cm	7.0 mg/l .008 mg/l/cm^2 .0003 mg/l/cm^2/hr	15.1 mg/l .017 mg/l/cm^2 .0004 mg/l/cm^2/hr	24.5 mg/l .027 mg/l/cm^2 .0004 mg/l/cm^2/hr
61.0 cm below Surface	<.5 mg/l <.001 mg/l/cm^2	7.5 mg/l .008 mg/l/cm^2 .0003 mg/l/cm^2/hr	15.4 mg/l .017 mg/l/cm^2 .0004 mg/l/cm^2/hr	23.6 mg/l .026 mg/l/cm^2 .0004 mg/l/cm^2/hr
AGITATED SYSTEM	<.5 mg/l <.001 mg/l/cm^2	7.1 mg/l .0008 mg/l/cm^2 .0003 mg/l/cm^2/hr	14.2 mg/l .016 mg/l/cm^2 .0003 mg/l/cm^2/hr	23.3 mg/l .026 mg/l/cm^2 .0004 mg/l/cm^2/hr

Volume of the test container was 60.83 liters.
Surface area of the test container was 907.92 cm^2.
Instrument fan positioned to blow air across water surface.

TABLE 2-3. CO_2 SORPTION - BUFFERED pH = 9

Time	Initial	20 Hours	44 Hours	50 Hours
STAGNANT SYSTEM				
5.1 cm below Surface	<.5 mg/1 <.001 mg/1/cm^2	2.1 mg/1 .002 mg/1/cm^2 .0001 mg/1/cm^2/hr	4.1 mg/1 .005 mg/1/cm^2 .0001 mg/1/cm^2/hr	5.6 mg/1 .006 mg/1/cm^2 .0001 mg/1/cm^2/hr
20.3 cm below Surface	<.5 mg/1 <.001 mg/1/cm^2	2.6 mg/1 .003 mg/1/cm^2 .0001 mg/1/cm^2/hr	3.0 mg/1 .003 mg/1/cm^2 .0001 mg/1/cm^2/hr	4.8 mg/1 .005 mg/1/cm^2 .0001 mg/1/cm^2/hr
40.6 cm below Surface	<.5 mg/1 <.001 mg/1/cm	1.9 mg/1 .002 mg/1/cm^2 .0001 mg/1/cm^2/hr	4.1 mg/1 .005 mg/1/cm^2 .0001 mg/1/cm^2/hr	5.0 mg/1 .006 mg/1/cm^2 .0001 mg/1/cm^2/hr
61.0 cm below Surface	<.5 mg/1 <.001 mg/1/cm^2	1.8 mg/1 .002 mg/1/cm^2 .0001 mg/1/cm^2/hr	4.8 mg/1 .005 mg/1/cm^2 .0001 mg/1/cm^2/hr	5.6 mg/1 .006 mg/1/cm^2 .0001 mg/1/cm^2/hr
AGITATED SYSTEM	<.5 mg/1 <.001 mg/1/cm^2	1.0 mg/1 .001 mg/1/cm^2 .0001 mg/1/cm^2/hr	2.2 mg/1 .002 mg/1/cm^2 <.0001 mg/1/cm^2/hr	2.8 mg/1 .003 mg/1/cm^2 .0001 mg/1/cm^2/hr

Volume of the test container was 60.83 liters.
Surface area of the test container was 907.92 cm^2.
Instrument fan positioned to blow air across water surface.

The experiments with a buffered pH 11 and an instrumentation fan blowing air across the test liquor surface resulted in a higher rate of carbon dioxide sorption. After 48 hours, CO_2 concentrations at 5.1 cm from the surface were 12.6 mg/ℓ for the case without the fan and 15.8 mg/ℓ for the run with the fan. The results at the other depth levels also confirm the increased sorption rate with the fan. The constant replenishment of CO_2 at the surface of the test medium by the fan accounts for the higher CO_2 sorption rate. The CO_2 sorption rate of the agitated system under these conditions was lower than the CO_2 sorption of both the agitated system of the previous experiment (nonbuffered pH 11) and the stagnant system under the same condition (buffered pH 11).

At pH 9, the rate of CO_2 sorption is quite low. At normal atmospheric carbon dioxide concentrations, carbon dioxide will equilibrate with an aqueous medium at a pH of approximately 8.3. Therefore, as the pH of an aqueous medium approaches 8.3, the rate of carbon dioxide sorption becomes slower due to the decreased driving force. The results of the pH 9 experiment, as compared to the other pH 11 experiments, indicate this to be the case. After approximately 50 hours, the CO_2 concentration at 5.1 cm below the surface for the pH 9 system was 5.6 mg/ℓ as compared to 15.8 mg/ℓ for the buffered pH 11 system. Other depth levels confirm the decreased sorption rate for the stagnant pH 9 system. The agitated pH 9 system showed a CO_2 concentration of only 2.8 mg/ℓ as compared to 14.2 mg/ℓ for the buffered pH 11 system after approximately 50 hours.

3.0 BENCH-SCALE SLUICING TESTS

Recent emphasis on water recycle/reuse in the electric power industry has induced power plants to investigate the feasibility of recycling water which has been used to sluice coal ash. This system is known as a closed-loop ash sluicing facility. The engineering involved in designing such a facility necessitates the prediction of scaling potentials of $CaCO_3$, $Mg(OH)_2$ and $CaSO_4 \cdot 2H_2O$ so that the system can be designed to control possible scaling problems. To predict scaling potentials for these species, the dissolution characteristics of the coal ash must be known. Therefore, it is important to investigate the ash dissolution characteristics which will be involved in such an ash handling facility. A bench-scale, closed-loop ash sluicing facility was built to study the dissolution characteristics of the ash in a system of this type. Measurements were made to determine the chemical composition of the water at various locations in the system. The values obtained will aid in the prediction of scaling potentials for $CaCO_3$, $Mg(OH)_2$, and $CaSO_4 \cdot 2H_2O$ in closed-loop ash sluicing facilities.

3.1 Technical Approach

A depiction of the laboratory scale ash sluicing facility which was built to simulate a closed-loop ash handling system is shown in Figure 3-1. Water from the settling pond was pumped to the mixing tank, a 6-liter (1.6 gal) Plexiglass cylinder where the coal ash is mixed with the sluice water. The slurry formed was allowed to flow by gravity from the mixing tank to the settling pond. An actual ash sluicing facility has a pipeline to the settling pond through which the ash slurry is pumped. The bench-scale model has such a pipeline simulation but this phase of the bench-scale model could not be used continuously because of flow stoppage due to plugging. The method of gravity flow from the mixing tank to the settling pond was adopted because dissolution occurs quickly in the mixing tank. Therefore, the majority of dissolution occurs in the mixing tank with only a minor fraction occurring in other portions of the system.

Batch dissolution studies indicate that the major portion of the dissolution of the ash occurs within 3 minutes and the mixing tank has a residence time of over 6 minutes. The sluice line of the bench-scale model from the mixing tank to the settling pond, simulating an actual sluice pipeline, was used during sampling routines to determine the effect upon chemical composition of the liquor caused by sluicing the ash slurry. Makeup water was fed into the mixing tank to simulate the replenishment of water lost from the system due to evaporation,

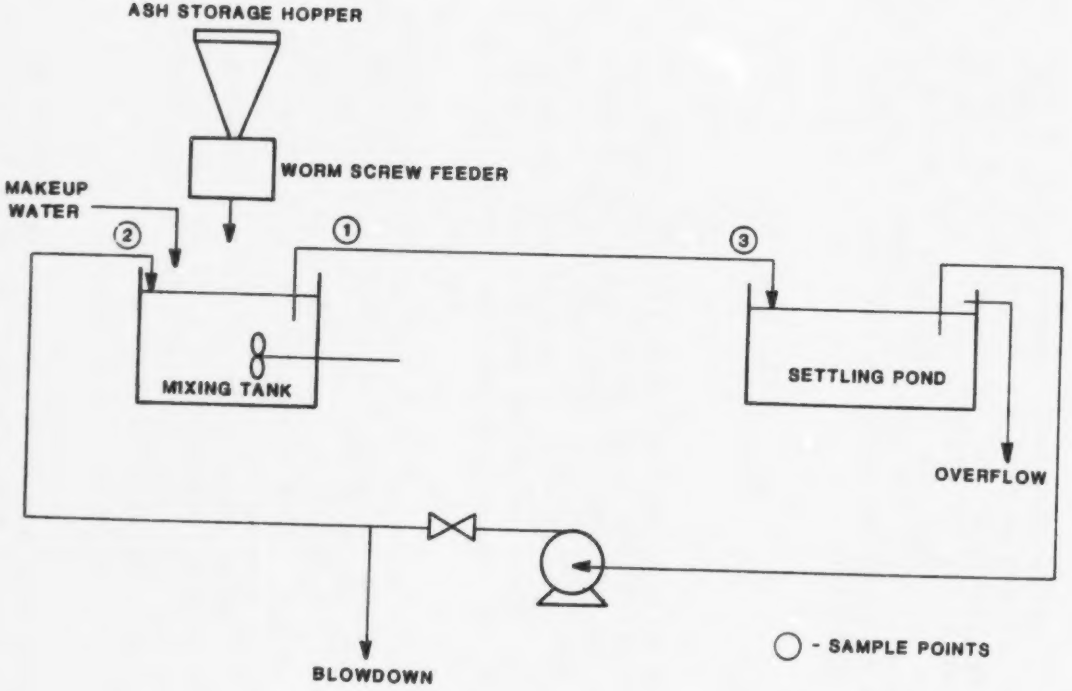


Figure 3-1. Bench-scale simulation model of ash pond facilities.

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leakage, or seepage. The chemical composition of this liquor varied among runs to simulate the composition of actual makeup water streams of the power plants studied. All of the liquid flows and/or slurries of the bench-scale model were controlled by peristaltic pumps. The fly ash was fed into the mixing tank by a Model SCR-20 precision volumetric screw feeder manufactured by Vibra Screw, Inc. The settling pond was constructed of fiberglass and had a capacity of 454ℓ (120 gal).

The liquor chemical compositions of the system must be determined at steady-state for values which can be effectively used in a computer model of the closed-loop ash sluicing facility. For the system to be at steady-state, the chemical composition of the liquor entering the mixing tank from the settling pond must be constant, and the chemical composition of the liquid flowing from the mixing tank to the settling pond must be constant. The equation

$$y_{out} = (y_o - y_{in})e^{-t/\tau} + y_{in}$$

describes the system surrounding the settling pond assuming no reaction occurs, where y_{out} is the concentration of the pond overflow, y_o is the initial pond overflow concentration, y_{in} is the inlet concentration to the pond, t is the number of hours the experiment has run, and τ is the residence time of the settling pond. This equation may be used to make a rough estimate for the time necessary for the system to reach steady-state.

The flow rates were controlled to produce a τ value of 10 hours. Chemical composition values should be approximately at steady-state at 30 hours, or $e^{-30/10}$, at which time $(y_o - y_{in})e^{-t/\tau}$ reduces to a negligible value such that essentially $y_{out} = y_{in}$. The experiments were conducted for five residence times of the settling pond to more realistically approach steady-state. More than three residence times will probably be necessary to achieve steady-state since the incoming stream of the settling pond is not constant as it is affected by the outgoing stream of the settling pond and precipitation and/or dissolution in the system.

Only one parameter was changed between runs using fly ash from any one of the plants. No more parameters were changed between runs so that correlations among runs could be made with confidence.

The samples collected were immediately measured for pH, temperature, and EMF using calcium and divalent cation-specific electrodes. Ionic activities of calcium and magnesium were calculated from graphs obtained from values gathered by measuring EMF values of calcium standards with the calcium and divalent cation-specific ion electrodes. Calcium and magnesium ionic activities along with the relative saturation of the species under investigation were also calculated by the chemical equilibrium computer program. Direct analytical methods were used to measure calcium, magnesium, sodium, total sulfate, and chloride concentrations of the samples which were collected. These samples were filtered, acidified, and diluted when collected. The carbonate concentrations of the various streams were measured by nondispersive infrared analysis. The carbonate samples collected were preserved using a NH_4OH-EDTA buffer system.

The tests were performed with fly ash collected from three coal-fired electric generating plants:

1) Comanche Steam Electric Station of Public Service Company of Colorado,
2) Four Corners Power Plant of Arizona Public Service, and
3) Plant Bowen of Georgia Power Company.

3.2 Experimental

3.2.1 Comanche Steam-Electric Station

Five experiments were performed using fly ash from the Comanche Steam-Electric Station. The initial experiment was performed using a makeup water approximating a probable makeup water stream at the Comanche plant, cooling tower blowdown.

The sulfate concentration of the makeup water was doubled for the second run. All other parameters remained the same.

The pH levels obtained during the first two runs were above the anticipated pH level of an ash sluicing system. An experimental run at a different pH value was desirable so that correlations could be drawn upon chemical compositions at varying pH values. Therefore, for the third run, a fan was used to blow air across the surface of the settling pond to try to increase the rate of carbon dioxide sorption and lower the pH of the system. The makeup water used during this run was identical to the makeup water of the first run.

The parameter change in the fourth experiment was to reduce the residence time of the mixing tank from 6.4 minutes to 3.2 minutes. The purpose of this adjustment was to determine if a decrease of the reaction time in the mixing tank would alter the chemical composition of the system.

A significantly lower pH value was obtained during the fifth run by bubbling an air stream spiked with carbon dioxide through the settling pond. The bubbler system was submerged only 2.5-7.6 cm (1-3 in) below the surface of the liquor of the settling pond to prevent agitation of the system which would probably cause additional ash dissolution in the settling pond. The carbon dioxide flow into the system was 1.0 ℓ/min.

3.2.2 Plant Bowen

The first experiment using Plant Bowen fly ash was performed at the conditions stated in Section 3.1, Technical Approach, and a makeup composition the same as the makeup water used in Comanche Steam-Electric Station Runs 1, 3, 4, and 5. The makeup water composition was not changed so that dissolution characteristics could be correlated among ashes from different plants, if deemed necessary.

The second experiment was run using the same makeup water composition as in the second Comanche fly ash run, which was twice the sulfate concentration of the makeup water of the first run. For the third Bowen run, water with a composition similar to that of the Bowen cooling tower blowdown was used as makeup.

The carbon dioxide bubbling system was used to reduce the pH of the settling pond for the fourth experiment using Plant Bowen coal ash. Carbon dioxide was bubbled through the settling pond at a rate of 0.5 ℓ/min.

3.2.3 Four Corners Power Plant

The first run using coal ash from the Four Corners Power Plant was performed using the same makeup water composition that was used for the first runs of the other plants. The makeup water composition simulated the chemical composition of the cooling tower blowdown stream of Comanche Steam-Electric Station. Other conditions of the experiments using Four Corners Power Plant coal ash were outlined in Section 3.1, Technical Approach.

The makeup water composition of the second experiment simulated the ash pond effluent of the Four Corners Power Plant. This stream would be a probable makeup water source for a sluicing facility at this plant. No other conditions were varied.

The third run had a makeup water composition which was the same as that of the first run using Four Corners Power Plant coal ash. The carbon dioxide bubbler was installed and carbon dioxide was bubbled through the surface of the settling pond at a rate of 0.5 ℓ/min.

3.3 Results

The experimental data gathered from the ash dissolution characterizations at steady-state appears in Appendix LA of this report. Operating conditions of each experiment also appear in these tables. Tables B-1, B-2, and B-3 in Appendix LB of this report contain the calcium concentrations of the sampled streams of each experiment. These values were used to determine if each run was at steady-state. Also included in Appendix LB are the parameters used to correlate the data from the three sets of runs.

3.4 Conclusions

3.4.1 Comanche Steam-Electric Station

Two plots were drawn to describe the dissolution of calcium in the mix tank of the bench-scale closed-loop ash sluicing facility. Figure 3-2 shows a graph describing the calcium dissolution as a function of the activity of the calcium ion. Figure 3-3 depicts the dissolution of calcium as a function of the activity product of calcium sulfate. It is important to note that towards the upper end of the graph (higher dissolution rates of calcium) the curve should begin to flatten out as the solubility product constant of calcium sulfate dihydrate ($K_{sp} = 2.4 \times 10^{-5}$ at 25°C) is approached due to the precipitation of gypsum.

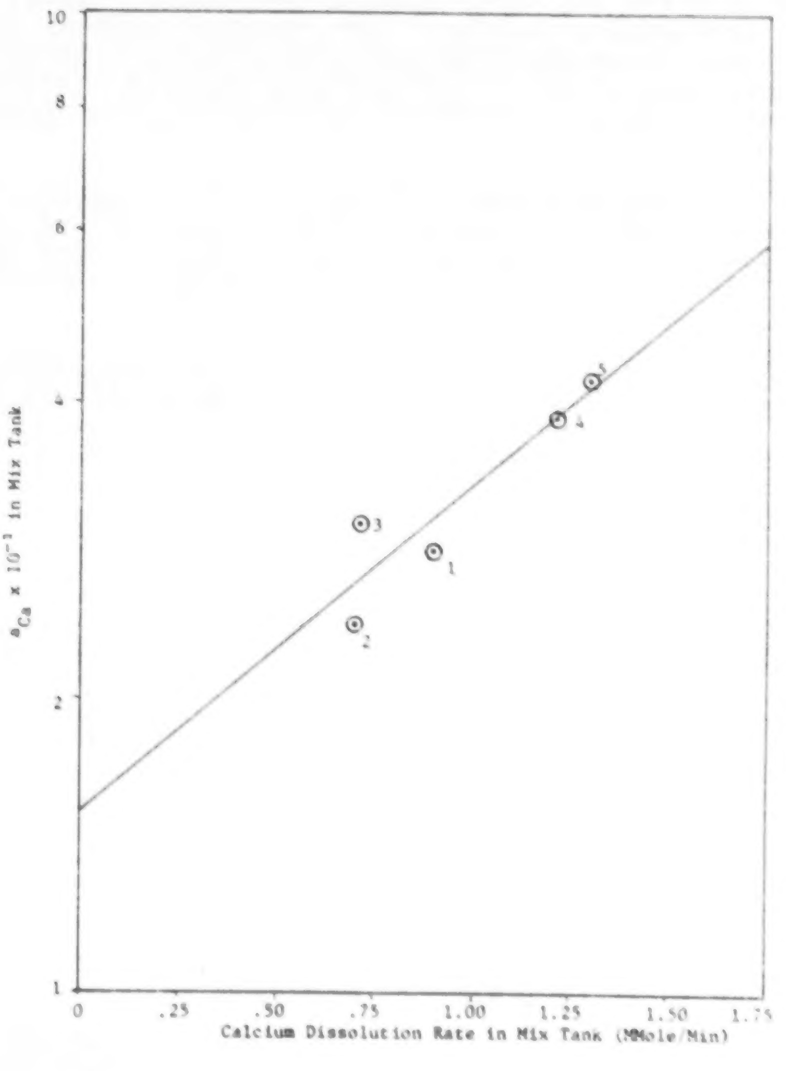

Figure 3-2. Comanche steam-electric station calcium dissolution rate in mix tank versus a_{Ca} in mix tank.

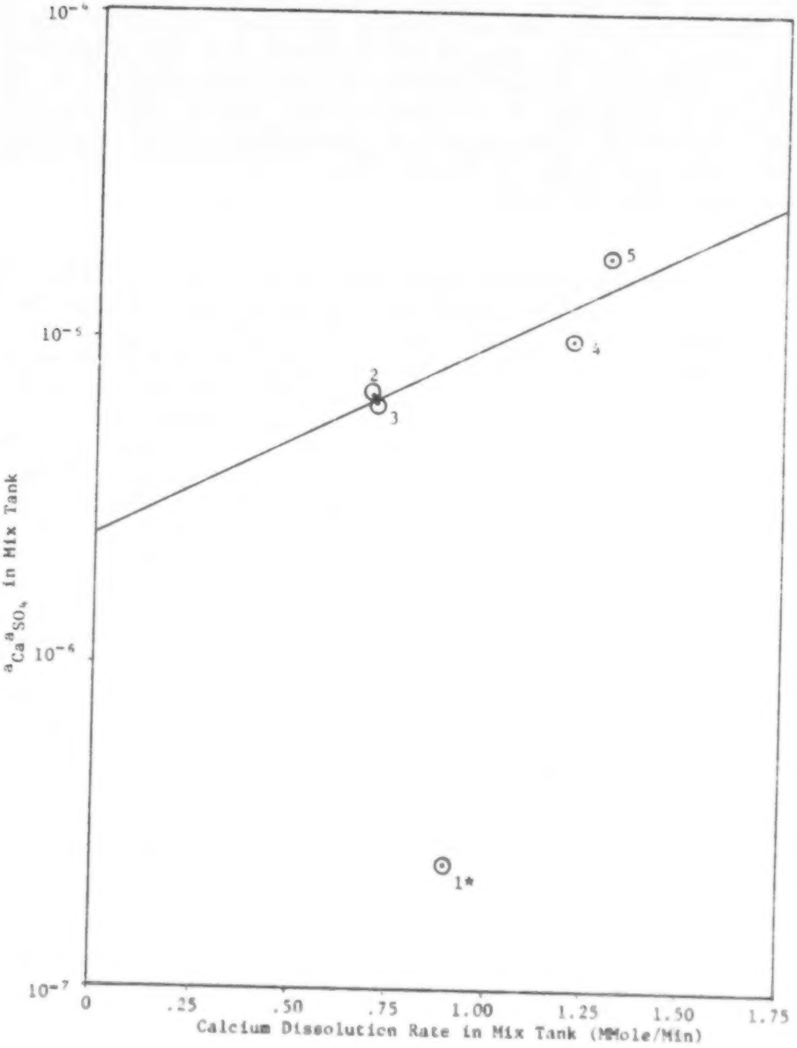

Figure 3-3. Comanche steam-electric station calcium dissolution rate in mix tank versus $a_{Ca}a_{SO_4}$ in mix tank.

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*Point inconsistent due to sulfate concentration not being at steady-state.

Sulfate dissolution was described basically in the same manner. Figure 3-4 is a plot of sulfate dissolution versus the activity of sulfate. Figure 3-5 shows the sulfate dissolution as a function of the activity product of calcium sulfate. The lesser slope of the graph of Figure 3-5 as compared to the graph of the calcium dissolution versus the activity product of calcium sulfate (Figure 3-3) indicates that sulfate arrives in the system primarily through the dissolution of calcium sulfate, whereas calcium arrives through the dissolution of calcium oxide as well as calcium sulfate.

Calcium carbonate precipitation in the mix tank as a function of the activity product of calcium carbonate in the mix tank is shown in Figure 3-6. The rate of precipitation of calcium carbonate was calculated as the rate of change of carbonate across the mix tank. This curve occurs in the range of relative saturation of 5-25 for calcium carbonate. The high relative saturation values are not primarily due to the carbonate concentration which is low, but to the rapid dissolution of calcium oxide and calcium sulfate and the resulting high calcium concentration which produces activity products of calcium carbonate well above the solubility product constant of calcium carbonate. The precipitation rate of calcium carbonate is not sufficient to reduce the concentration of calcium in the system such that the relative saturation of calcium carbonate would be close to one. The point associated with the first run is high and inconsistent with the others because the carbonate concentration of the settling pond had not reached steady-state. Analysis of the tap water used to fill the pond provided a carbonate concentration of 0.38 mmoles/ℓ. This value is considerably higher than the carbonate concentrations of the experiments with the exceptions of the first run and the fifth run which had the carbon dioxide bubbler installed. The carbonate concentration of the tap water approximates the final carbonate concentration of the settling pond of the first run indicating that calcium carbonate precipitation had not diminished the carbonate concentration to steady-state conditions.

Although the mixing tank is supersaturated with respect to magnesium hydroxide, this is not due to the presence of high concentrations of magnesium but to the high concentrations of hydroxide. Therefore, magnesium hydroxide will precipitate even with values of magnesium which are too low to calculate accurate dissolution rates. However, the amount of magnesium hydroxide which would precipitate is insignificant. The fifth run had a lower pH which increased the magnesium dissolution. The streams were still supersaturated with respect to $Mg(OH)_2$ but the amount of magnesium hydroxide which would precipitate still would not be substantial.

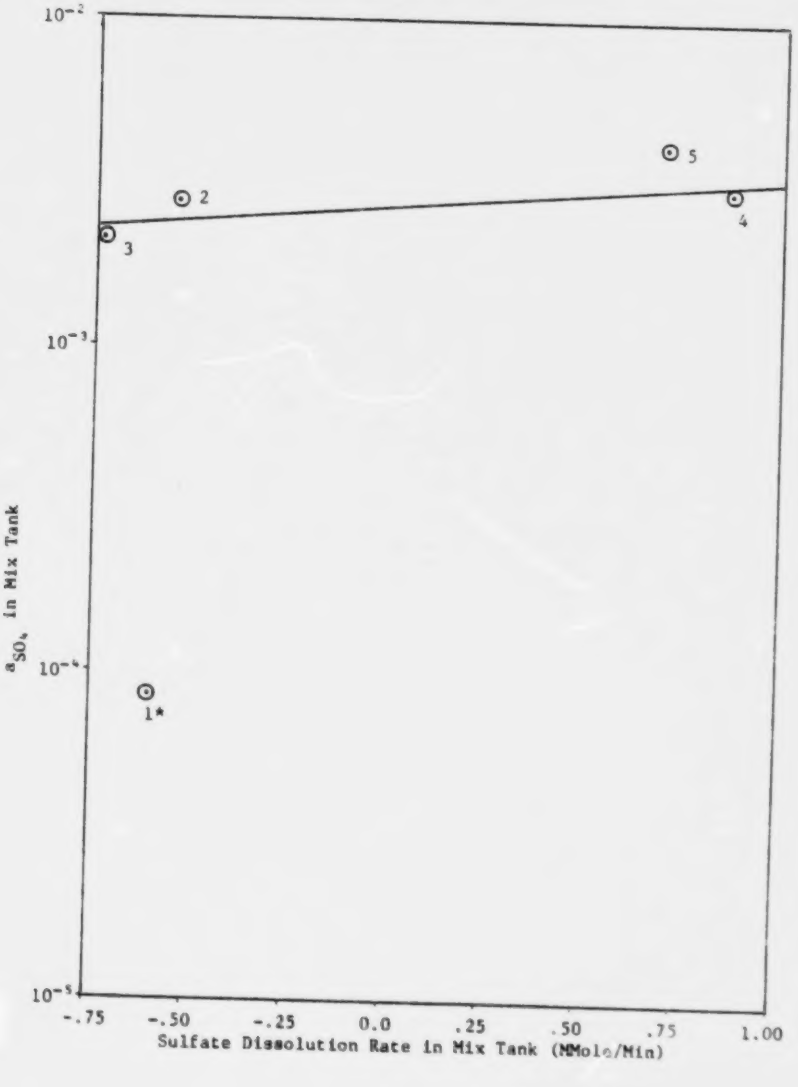

Figure 3-4. Comanche steam-electric station sulfate dissolution rate in mix tank versus a_{SO_4} in mix tank.

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*Point inconsistent due to sulfate concentration not being at steady-state.

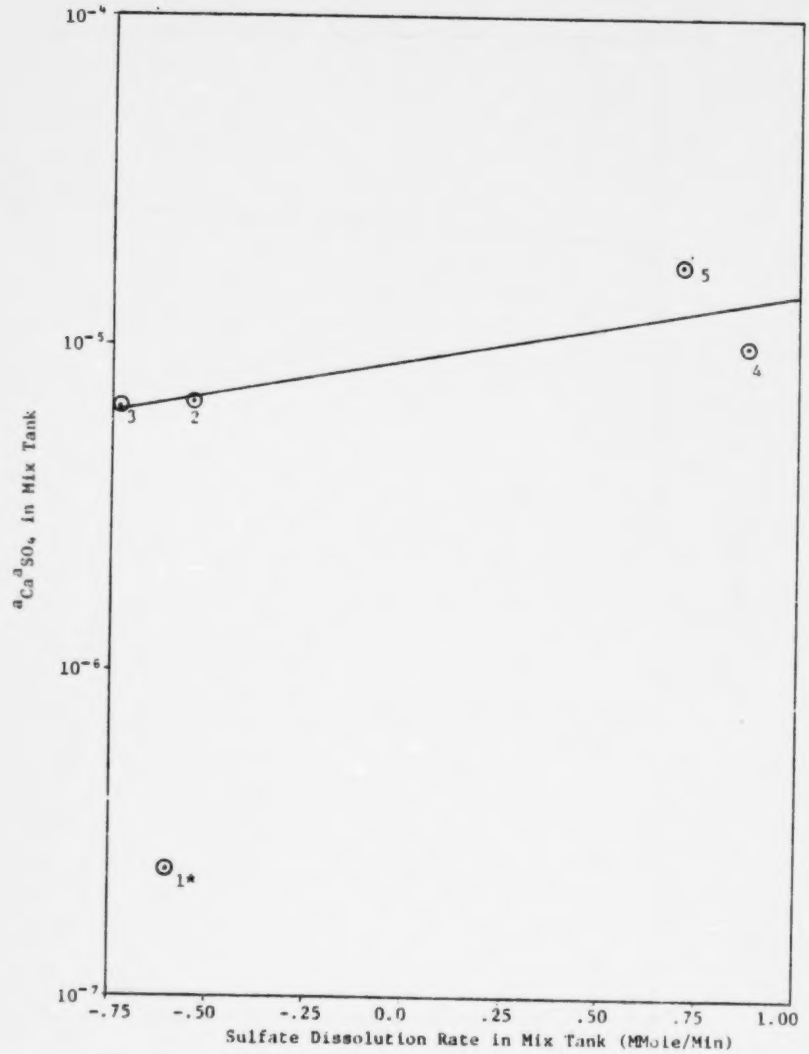

Figure 3-5. Comanche steam-electric station sulfate dissolution rate in mix tank versus $a_{Ca}a_{SO_4}$ in mix tank.

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*Point inconsistent due to sulfate concentration not being at steady-state.

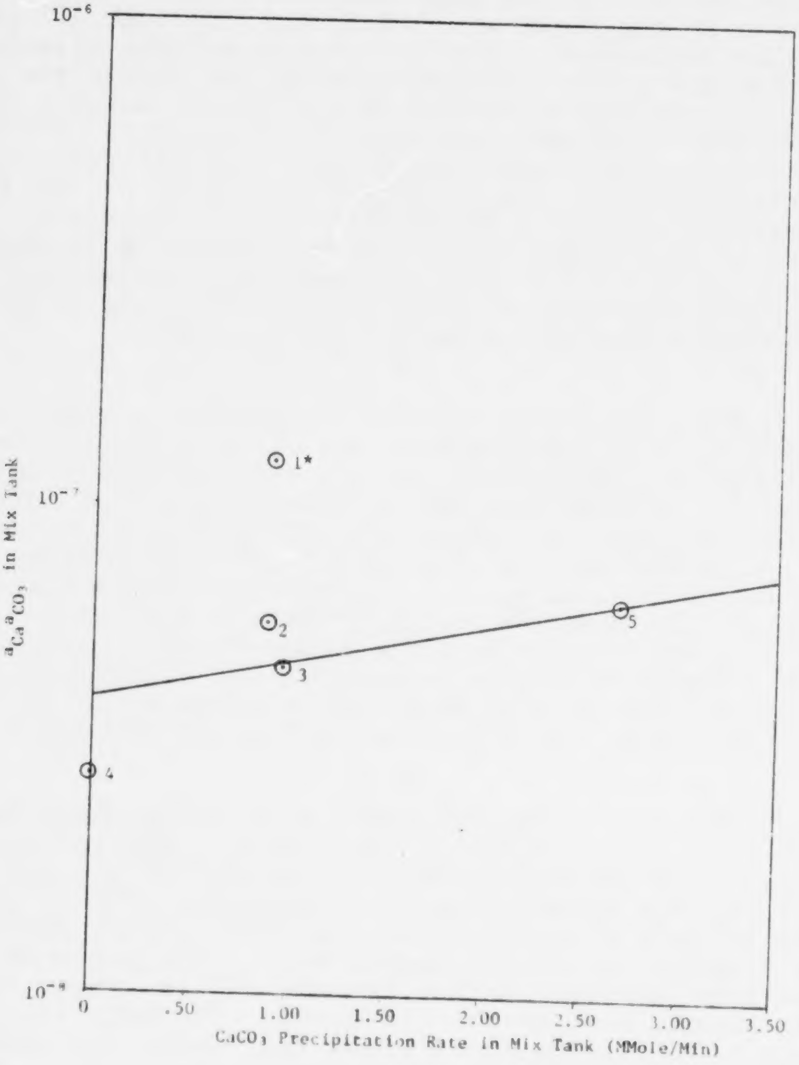

Figure 3-6. Comanche steam-electric station $CaCO_3$ precipitation rate in mix tank versus $a_{Ca}a_{CO_3}$ in mix tank.

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*Point inconsistent due to carbonate not being at steady-state.

The fourth run using Comanche Steam-Electric Station coal ash had a reduced residence time in the mix tank, from 6.4 minutes to 3.2 minutes. The sulfate dissolution in the mix tank during the fourth run was significantly higher than the sulfate dissolution in the first and third runs although all three runs had similar parameters. The fourth run sulfate dissolution was higher than the sulfate dissolution of the second run which had a higher sulfate concentration in the makeup water. Specifically, the first and third runs had negative dissolution rates, about -0.6 mmole/min. This was due primarily to calcium sulfate dihydrate precipitation. The sulfate dissolution of the fourth run was a positive rate of 0.88 mmole/min. The increase in dissolution rate of the fourth run could be misleading in that the increase was probably not an increase in the dissolution rate of sulfate but a decrease in the precipitation rate of gypsum due to the shorter residence time in the mix tank.

The dissolution rate of calcium in the mix tank of the fourth run was greater than the dissolution rate of calcium in the first and third runs but the difference was not as significant as the increase in the dissolution rate of sulfate. This is due to the fact that there are two sources of calcium available for dissolution, CaO and $CaSO_4$. The two sources allow calcium to enter the system at a faster rate than sulfate. This accounts for the positive calcium dissolution rates of the first three runs even though the dissolution rates of sulfate were negative. The fact that all the runs had higher calcium dissolution rates than sulfate dissolutiion rates supports the fact that CaO and $CaSO_4$ are both readily available sources of calcium.

The fifth run also had higher calcium and sulfate dissolution rates than the first three runs. The increase in dissolution was probably caused by the lower pH of the system. Noting that the calcium dissolution rate approximates that of the fourth run, the sulfate dissolution of the fifth run is lower than the sulfate dissolution of the fourth run. This could be due to additional gypsum precipitation because of the longer residence time of the mix tank in the fifth run. However, if this were the cause, the calcium dissolution rate would not approximate that of the fourth run due to gypsum precipitation. The reason that there is a greater difference between the calcium dissolution rate and the sulfate dissolution of the fifth run as compared to the fourth run, is that lower pH values enhance the potential to dissolve calcium oxide more than calcium sulfate.

There are indications that the first run using Comanche Steam-Electric Station coal ash was not at steady-state with respect to sulfate even though sampled at three residence times of the settling pond as described in Section 3.1. The first run had fresh water in the settling pond whereas the water of the settling pond was not renewed between runs using the same coal ash. The fresh water has a lower pH, and, as stated in the previous paragraph, there is a greater potencial to dissolve CaO as opposed to $CaSO_4$ at lower pH values. Initial higher concentrations of calcium would tend to impede calcium sulfate dissolution, requiring more time to reach steady-state.

Table B-4 of Appendix LB of this report contains the information which was used to derive the graphs which describe the dissolution of Comanche Steam-Electric Station coal ash.

3.4.2 Plant Bowen

Four graphs were drawn to describe the dissolution and/or precipitation rates occurring in the mix tank of the four runs using Plant Bowen coal ash. Figure 3-7 is a plot of the calcium dissolution in the mix tank versus the activity of the calcium in the mix tank, and Figure 3-8 is a plot of the sulfate dissolution in the mix tank versus the activity of sulfate in the mix tank. Figure 3-9 is a plot of the sulfate dissolution of the mix tank, which approximates the calcium sulfate dissolution since calcium sulfate is the major source of sulfate from the ash, versus the activity product of calcium sulfate. The entire curve is above the solubility product constant of calcium sulfate dihydrate ($K_{sp} = 2.4 \times 10^{-5}$ at 25°C). Calcium sulfate dihydrate would not dissolve at these conditions yet the curve indicates an increase in dissolution above the solubility product constant of calcium sulfate dihydrate. An explanation is that the calcium sulfate of the ash is not in the form of calcium sulfate dihydrate. There are several other forms of calcium sulfate which are considerably more soluble than calcium sulfate dihydrate. Two are α-$CaSO_4$ and α-$CaSO_4 \cdot \frac{1}{2}H_2O$. These two forms have solubilities of 0.63 to 0.8 grams per 100 milliliters of solution, whereas calcium sulfate dihydrate has a solubility of 0.2 to 0.22 grams per 100 milliliters of solution.[1] These values and Figure 3-9 indicate that the calcium sulfate is present in one of the more soluble forms which dissolves in the mix tank. Solids analysis by X-ray diffraction was not attempted since the sulfate solids represent only a small fraction of the total solids present.

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[1] GM-061: Gmelin, Gmelin Handbuch de anorg. Chemie, 8. Auflage, Calcium, Tiel B. Lieferung 3, (1961).

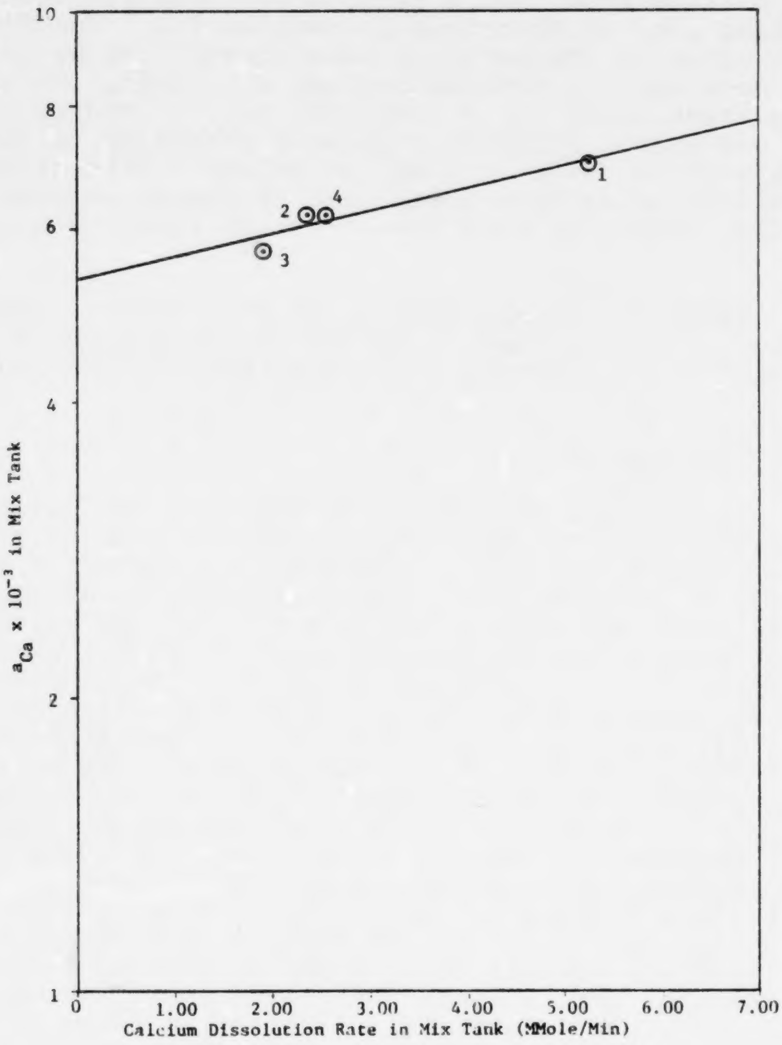

Figure 3-7. Plant Bowen calcium dissolution rate in mix tank versus a_{Ca} in mix tank.

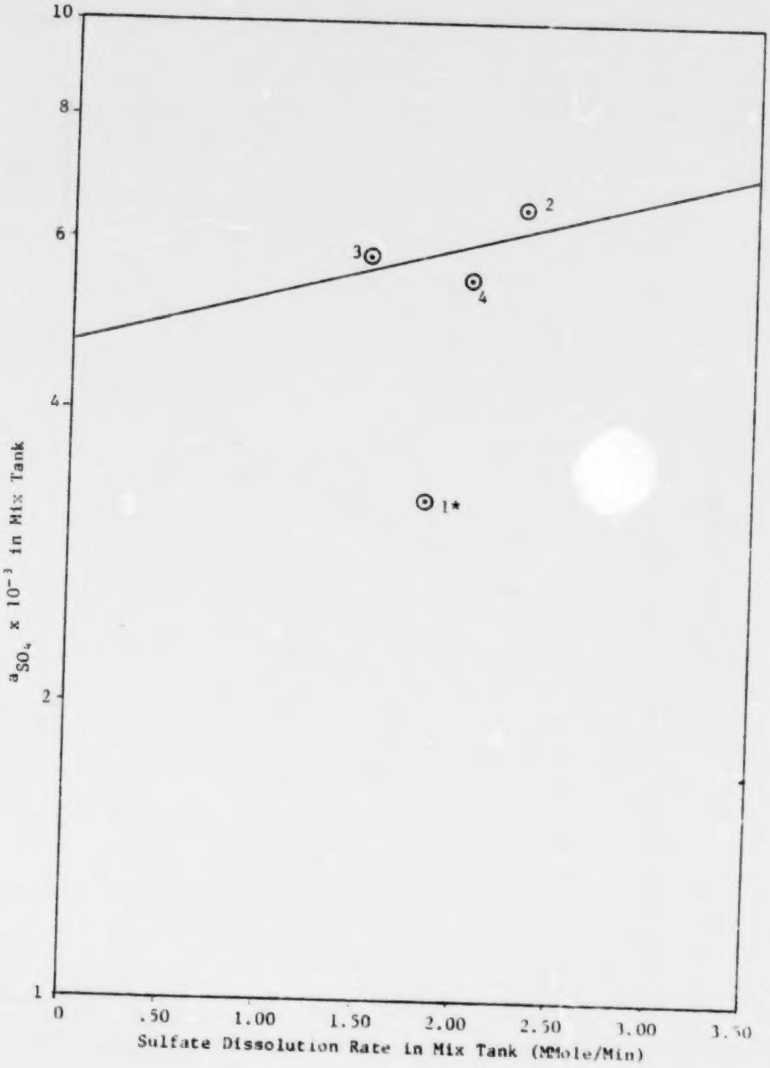

Figure 3-8. Plant Bowen sulfate dissolution rate in mix tank versus a_{SO_4} in mix tank.

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*Point inconsistent due to sulfate concentration not being at steady-state.

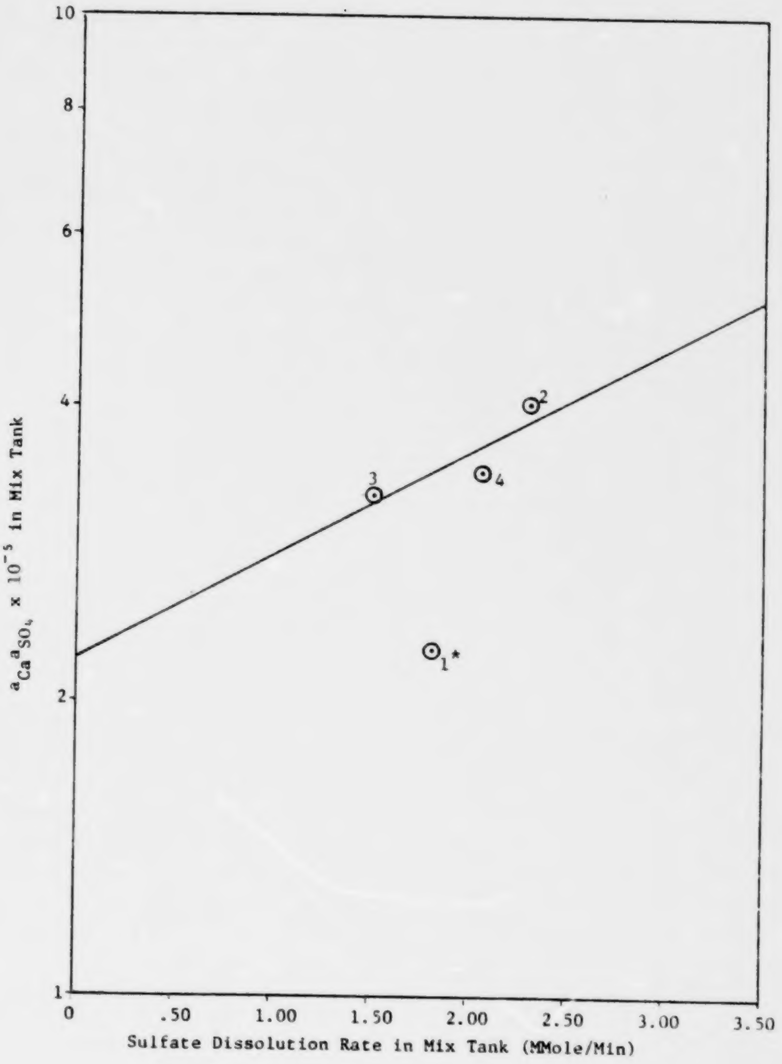

Figure 3-9. Plant Bowen sulfate dissolution rate in mix tank versus $a_{Ca}a_{SO_4}$ in mix tank.

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*Point inconsistent due to sulfate concentration not being at steady-state.

Figure 3-10 is a plot of the calcium carbonate precipitation rate in the mix tank versus the activity product of calcium carbonate. As in the Comanche Steam-Electric Station ash dissolution characterization experiments, the curve appears in the range of relative saturation values for calcium carbonate of 10-30. The precipitation of calcium carbonate is insufficient to reduce the ionic activity of calcium to a level where the solubility product of calcium carbonate will approach the solubility product constant of calcium carbonate.

The majority of the streams were supersaturated with magnesium hydroxide in all of the experiments with Plant Bowen coal ash. The activity product of magnesium hydroxide was above the solubility product constant of magnesium hydroxide due to high hydroxide concentrations even with low magnesium concentrations. Therefore, even though many streams were supersaturated with respect to magnesium hydroxide, there is no potential scaling problem because the magnesium concentrations are too low to allow substantial magnesium hydroxide precipitation.

Table B-5 of Appendix LB of this report contains the information used to derive the graphs which describe the dissolution of Plant Bowen coal ash.

3.4.3 Four Corners Power Plant

Three experiments were performed with coal ash from the Four Corners Power Plant. However, dissolution rates were too low to plot any data over a sufficient range. If this data were plotted over an insufficient range, erroneous graphs could possibly be drawn. Therefore, since the dissolution of the ash could not be illustrated with certainty, graphs were not used to depict the dissolution of fly ash from Four Corners Power Plant. The only species that could possibly present a scaling problem is calcium carbonate. All the streams in all of the experiments were supersaturated with respect to calcium carbonate. This is due primarily to the extremely low solubility of calcium carbonate. The concentrations of calcium were relatively low as compared to calcium concentrations from other plants. Carbonate concentrations were somewhat higher due apparently to carbonate available from the fly ash. Still the low concentrations and meager dissolution rates of calcium prevent the creation of a scaling problem. All of the streams of all of the runs were subsaturated with respect to calcium sulfate dihydrate and magnesium hydroxide.

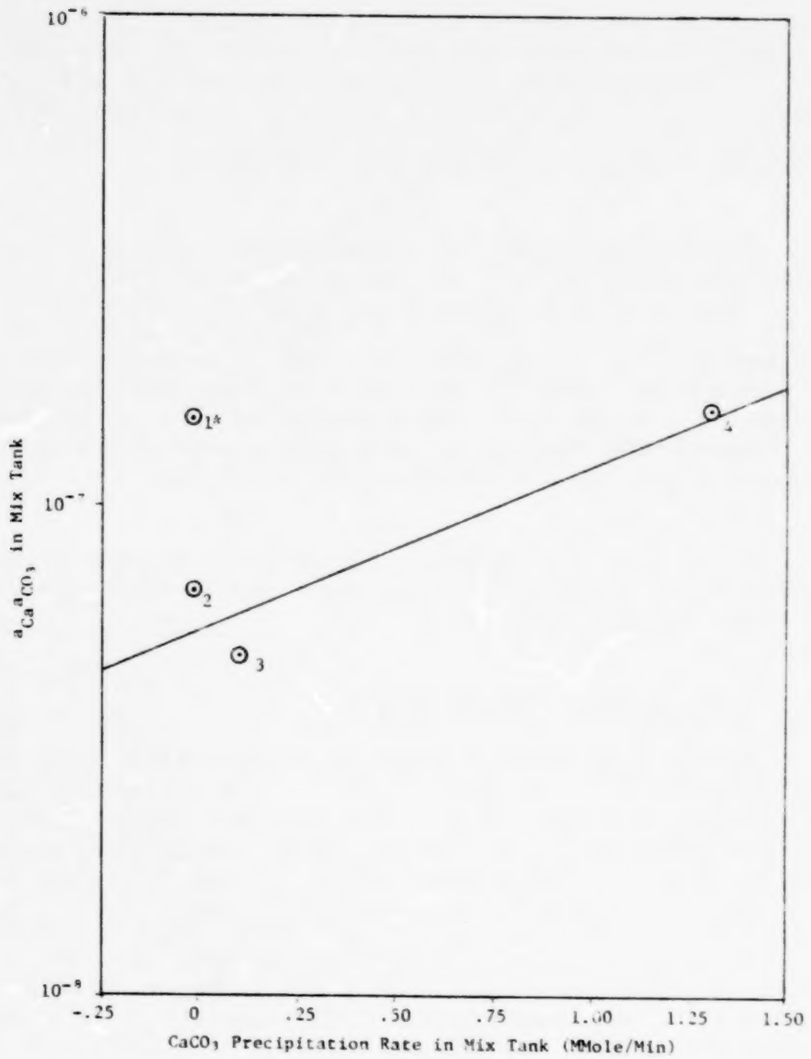

Figure 3-10. Plant Bowen $CaCO_3$ precipitation rate in mix tank versus $a_{Ca}a_{CO_3}$ in mix tank.

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*Point inconsistent due to carbonate concentration not being at steady-state.

4.0 BATCH DISSOLUTION AND LEACHING TESTS

In conjunction with the bench-scale studies, batch dissolution characterizations and leaching studies of the coal ash were conducted. The leaching studies were performed to determine the amount of alkalinity available from each of the coal ashes tested and the concentrations of several chemical species dissolved from the coal ashes at various pH conditions. The batch dissolution characterization experiments were conducted to gain information concerning liquor composition effects in simple laboratory tests which may correlate to the information gathered from the ash dissolution characterization studies so that information desired for computer modeling could be derived by this simpler method. Liquor pH values were adjusted periodically in the leaching experiments but no pH control was exerted for the batch dissolution experiments.

Realistically, these tests will not be able to provide the total information necessary for a computer model of a closed-loop ash sluicing facility. But a favorable correlation of the batch dissolution characterizations could reduce the number of runs of the bench-scale closed-loop ash sluicing facility necessary to model an ash sluicing facility. Even though the results of the batch dissolution characterizations and the ash dissolution characterizations will be compared, values obtained by the batch dissolution characterizations were not used in the computer models. The results of the experiments did not cover a large enough variation in operating and ash parameters to justify correlation by a computer model.

The purpose of this subtask was not to ascertain if favorable correlations exist such that the information gathered through the batch dissolution characterizations could justifiably be used to computer-model a closed-loop ash sluicing facility. The batch dissolution characterizations were conducted to gather the information available by performing experiments of this type and to have a data bank available so that correlations could be attempted between the two sources of information.

4.1 Technical Approach

4.1.1 Ash Leaching

To determine the available alkalinity and the rate of dissolution of that alkalinity from the coal ashes, the coal ashes were subjected to liquors of varying pH. The pH of the liquor was held constant by the addition of acid. The equivalents of acid added were recorded as was the time of the addition. In this manner, the available alkalinity of the respective fly ashes, present predominantly as CaO and MgO, can be determined as a function of pH and time. Analyses for calcium, magnesium, sodium, potassium and total sulfate were performed on resulting liquors which were collected after all available alkalinity had been leached.

The ash leaching studies as well as the batch dissolution characterizations were performed with fly ash collected from the following three plants:

1) Comanche Steam-Electric Station of Public Service Company of Colorado,

2) Plant Bowen of Georgia Power Company, and

3) Four Corners Power Plant of Arizona Public Service.

4.1.2 Batch Dissolution

The batch dissolutions were performed by varying the chemical composition of the test liquors to which the coal ashes were subjected. pH, EMF readings of calcium and divalent cation specific ion electrodes, and time were monitored continuously using a chart recorder. These values are presented in Appendix LC of this report. The EMF values obtained were used to calculate the ionic activities of calcium and magnesium. EMF readings were taken of standard solutions and used to derive standard curves. The EMF readings recorded during the tests were then used to calculate ionic activities from these graphs. Each final sample was analyzed for calcium, magnesium, sodium, total sulfate and chloride. Samples were also taken at 10 and 20 minutes into the experiment, and analyzed for calcium and magnesium. The temperatures of the solutions were also recorded to determine if the reactions involved were endothermic or exothermic to such a degree as to effect the temperature of the system. With the information gathered, the dissolution properties of calcium and magnesium of the coal ashes can be interpreted as a function of chemical composition and pH.

4.2 Experimental

4.2.1 Ash Leaching

The leaching experiments were performed in 400-ml beakers. A magnetic stirring bar and a mechanical stirrer were used to mix the slurry. The experiments which called for a 7% slurry were a combination of 186 grams of water and 14 grams of the coal ash. A 2% slurry was formed by combining 196 grams of water and 4 grams of the coal ash. The electrodes were positioned in the test liquor, the coal ash added and, as quickly as possible thereafter, the pH was adjusted by addition of hydrochloric acid of known concentration. The test reactor was covered to prevent the effects on pH caused by the sorption of carbon dioxide. The desired pH was maintained by the repeated addition of acid as necessary. The amount of acid added and the time of addition were recorded with each pH adjustment. The experiment was conducted until all available alkalinity had been leached. Fly ash from the Four Corners Power Station was examined at pH levels of 3.0, 6.0, and 8.5 with a 7% slurry of ash and water, and at pH levels 3.0 and 8.5 with a 2% slurry. pH values of 6.0, 8.5 and 10.4 were used to describe the Plant Bowen fly ash using a 7% slurry. Fly ash collected from Comanche Steam-Electric Station was examined using a 7% ash slurry and pH values of 6.0 and 8.5.

4.2.2 Batch-Dissolution

Five chemical compositions were used as the aqueous media in the experiments for the batch dissolution characterizations. In this report, the chemical compositions are identified by run number as follows:

Run No. 1 - Deionized water

Run No. 2 - A 1:1 mixture of deionized water and the resultant liquor of Run No. 1. (Therefore, the initial concentrations of the second run were one-half of the final concentrations of the first run.)

Run No. 3 - 25 ppm carbonate (0.417 mmole/ℓ)
500 ppm sulfate (5.21 mmole/ℓ)
259 ppm sodium (11.3 mmole/ℓ)

Run No. 4 - 25 ppm carbonate (0.417 mmole/ℓ)
2500 ppm sulfate (26.0 mmole/ℓ)
1220 ppm sodium (52.8 mmole/ℓ)

Run No. 5 - 100 ppm carbonate (1.67 mmole/ℓ)
500 ppm sulfate (5.21 mmole/ℓ)
316 ppm sodium (13.8 mmole/ℓ)

Each coal ash was examined using each of the test liquors listed above monitoring pH and EMF values for calcium and divalent cation specific ion electrodes using a chart recorder. Separate runs were necessary for each species so that the information could be continuously recorded using the strip chart recorder. The 10-minute sample was taken from the calcium specific ion electrode run, the 20-minute sample from the divalent cation specific ion electrode; and the 30-minute sample was taken at the end of the pH run. The samples were taken in this manner to interface the three runs necessary. For each of the three ashes tested, a 7% mixture of the ash and the test liquor was used. During the divalent cation experiments, the temperature of slurry was measured and recorded. Calcium standards were analyzed after each run involving a specific ion electrode so that the EMF values obtained could be used to draw graphs from which ionic activities for calcium and magnesium could be determined.

4.3 Results

Tables 4-1, 4-2, and 4-3 contain the results of the ash leaching studies. Table 4-4 presents the amount of leachable species at pH 6 as a percent of the ash. The results of the batch dissolution studies are shown in Table 4-5.

4.4 Conclusions

4.4.1 Ash Leaching

4.4.1.1 Comanche Steam-Electric Station

The leaching studies of coal ash from Comanche Steam-Electric Plant show that calcium and sulfate are the major species leached. Magnesium and sodium are less significant constituents (see Table 4-1). The sulfate to calcium ratio of the leaching results is 0.172 for pH 6.0 and 0.154 for pH 8.5. These values indicate that the calcium dissolving into the system arrives predominantly as CaO, the remaining calcium arriving as $CaSO_4$.

TABLE 4-1. RESULTS OF CHEMICAL ANALYSIS FROM LEACHING OF ASH SAMPLES AT CONSTANT pH FOR COMANCHE STEAM-ELECTRIC STATION

	Prec. Ash[1] pH 6.0 (mmole/ℓ)[3]	Prec. Ash[1] pH 8.5 (mmole/ℓ)[3]
Calcium	53.9	42.2
Magnesium	3.5	1.6
Sodium	1.3	1.0
Potassium	--	.11
Sulfate	9.28	6.50

[1] Maintained pH of 6.0 by adding HCl.

[2] Maintained pH of 8.5 by adding HCl.

[3] All values represent mmole/ℓ of soluble species in leachate after 14 grams of ash were leached in 186 grams of deionized water at constant pH.

TABLE 4-2. RESULTS OF CHEMICAL ANALYSIS FROM LEACHING OF ASH SAMPLES AT CONSTANT pH FOR PLANT BOWEN

	Prec. Ash[1] pH 6.0 (mmole/ℓ)[4]	Prec. Ash[2] pH 8.5 (mmole/ℓ)[4]	Prec. Ash[3] pH 10.4 (mmole/ℓ)[4]
Calcium	24.2	14.2	10.5
Magnesium	.23	.06	.01
Sodium	3.0	1.1	1.3
Potassium	.90	.72	.56
Sulfate	10.0	9.22	7.71

[1] Maintained pH of 6.0 by adding HCl.

[2] Maintained pH of 8.5 by adding HCl.

[3] Maintained pH of 10.4 by adding HCl.

[4] All values represent mmole/ℓ of soluble species in leachate after 14 grams of ash were leached in 186 grams of deionized water at constant pH.

TABLE 4-3. RESULTS OF CHEMICAL ANALYSIS FROM LEACHING OF ASH SAMPLES AT CONSTANT pH FOR FOUR CORNERS POWER STATION

	Prec. Ash[1] pH 3.0 (mmole/ℓ)[6]	Prec. Ash[2] pH 6.0 (mmole/ℓ)[6]	Prec. Ash[3] pH 8.5 (mmole/ℓ)[6]	Prec. Ash[4] pH 3.0 (mmole/ℓ)[7]	Prec. Ash[5] pH 8.5 (mmole/ℓ)[7]
Calcium	15.5	13.4	11.7	4.52	3.02
Magnesium	.23	.10	.07	.07	.01
Sodium	.52	.48	.48	.12	.08
Potassium	.12	.06	.04	.04	<.02
Sulfate	1.2	.31	.56	.08	.01

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[1] Maintained pH of 3.0 by adding HCl.

[2] Maintained pH of 6.0 by adding HCl.

[3] Maintained pH of 8.5 by adding HCl.

[4] Maintained pH of 3.0 by adding HCl.

[5] Maintained pH of 8.5 by adding HCl.

[6] All values represent mmole/ℓ of soluble species in leachate after 14 grams of ash were leached in 186 grams of deionized water at constant pH.

[7] All values represent mmole/ℓ of soluble species in leachate after 4 grams of ash were leached in 196 grams of deionized water at constant pH.

TABLE 4-4. LEACHABLE SPECIES FROM ASH SAMPLES AT pH 6[1]

Species[2]	Comanche (wt. % of ash)	Bowen (wt. % of ash)	Four Corners (wt. % of ash)
CaO	3.3	1.0	1.0
MgO	0.2	0.01	0.006
Na_2O	0.4	0.10	0.04
K_2O	--	0.06	0.004
$CaSO_4$	1.7	1.8	0.06

---

[1] Experiments performed with a 1% slurry with pH adjusted periodically to 6.0.

[2] All sulfate is assumed to enter the system as $CaSO_4$.

TABLE 4-5. ASH DISSOLUTION CHARACTERIZATIONS - BATCH DISSOLUTIONS

	C-1(30 min)	C-2(30 min)	C-3(30 min)	C-4(30 min)	C-5(30 min)
Calcium	6.18	6.73	2.12	0.96	4.26
Magnesium	0.002	0.004	0.002	0.002	0.002
Sodium	0.78	1.24	11.5	56.5	13.7
Sulfate	0.666	0.649	0.627	18.1	4.36
Chloride	0.259	0.397	0.138	0.138	0.144
Carbonate	0.14	0.08	0.20	0.24	0.16
pH	11.9	12.0	12.0	12.0	11.9
T, °F	74.5	75.8	75.5	74.5	75.0
a_{Ca}	1.67×10^{-3}	1.60×10^{-3}	7.0×10^{-4}	4.2×10^{-4}	4.0×10^{-4}
a_{Mg}	3.3×10^{-4}	8.0×10^{-4}	7.0×10^{-4}	9.5×10^{-4}	1.68×10^{-3}
a_{Ca}[1]	3.20×10^{-3}	3.32×10^{-3}	1.04×10^{-3}	2.48×10^{-4}	1.76×10^{-3}
a_{Mg}[1]	4.15×10^{-7}	6.73×10^{-7}	3.40×10^{-7}	2.62×10^{-7}	3.70×10^{-7}

	B-1(30 min)	B-2(30 min)	B-3(30 min)	B-4(30 min)	B-5(30 min)
Calcium	10.3	15.1	10.6	10.6	9.62
Magnesium	0.010	0.014	0.010	0.012	0.008
Sodium	1.19	1.79	11.4	52.9	13.5
Sulfate	9.38	14.1	14.8	35.4	14.9
Chloride	0.586	0.952	0.327	0.358	0.400
Carbonate	0.16	0.26	0.28	0.32	0.27
pH	10.8	10.8	10.8	10.7	10.8
T, °F	76.5	77.8	72.7	73.3	74.0
a_{Ca}	1.97×10^{-3}	3.46×10^{-3}	1.35×10^{-3}	3.80×10^{-3}	1.28×10^{-3}
a_{Mg}	7.8×10^{-4}	3.2×10^{-4}	1.29×10^{-3}	---	1.82×10^{-3}
a_{Ca}[1]	3.95×10^{-3}	5.05×10^{-3}	3.41×10^{-3}	2.36×10^{-3}	3.06×10^{-3}
a_{Mg}[1]	3.65×10^{-6}	4.51×10^{-6}	3.17×10^{-6}	2.79×10^{-6}	2.50×10^{-6}

	F-1(30 min)	F-2(30 min)	F-3(30 min)	F-4(30 min)	F-4(30 min)
Calcium	4.43	4.71	3.98	5.15	3.20
Magnesium	0.008	0.005	0.004	0.003	0.010
Sodium	0.59	0.80	10.8	53.8	13.4
Sulfate	0.972	1.61	6.00	26.3	5.42
Chloride	0.045	0.090	0.115	0.110	0.118
Carbonate	0.21	0.16	0.11	0.15	0.28
pH	11.7	11.6	11.7	11.8	11.7
T, °F	74.2	75.8	74.2	74.9	76.0
a_{Ca}	1.10×10^{-3}	1.05×10^{-3}	9.0×10^{-4}	8.4×10^{-4}	6.1×10^{-4}
a_{Mg}	9.5×10^{-4}	8.0×10^{-4}	3.5×10^{-4}	9.9×10^{-4}	6.7×10^{-4}
a_{Ca}[1]	2.43×10^{-3}	2.51×10^{-3}	1.61×10^{-3}	1.22×10^{-3}	1.28×10^{-3}
a_{Mg}[1]	2.22×10^{-6}	1.47×10^{-6}	9.47×10^{-7}	4.61×10^{-7}	2.24×10^{-6}

Explanation of Sample Headings

C - denotes Comanche Steam-Electric Station
F - denotes Four Corners Power Plant
B - denotes Plant Bowen

Integer denotes the run number (see below)

Time indicates the time of the run at which the sample was taken.

Run #1 - 7% Slurry	D.I. Water
Run #2 - 7% Slurry	1:1 D.I. Water - Liquor from Run #1
Run #3 - 7% Slurry	25 ppm CO_3-500 ppm SO_4
Run #4 - 7% Slurry	25 ppm CO_3-2500 ppm SO_4
Run #5 - 7% Slurry	100 ppm CO_3-500 ppm SO_4

25 ppm CO_3 = 0.417 mmole/ℓ CO_3
100 ppm CO_3 = 1.67 mmole/ℓ CO_3
500 ppm SO_4 = 5.21 mmole/ℓ SO_4
2500 ppm SO_4 = 26.0 mmole/ℓ SO_4

[1] Ionic activities calculated by chemical equilibrium program.

Since the magnesium and sodium concentrations are not significant, the sulfate concentration is the result mainly of $CaSO_4$ dissolution as shown in Table 4-4.

The plot of meq acid/g fly ash versus time (Figure 4-1) obtained from the data gathered during the leaching studies of Comanche Steam-Electric Station ash show that at pH 6.0, 1.60 meq OH^-/g ash or 22.4 milliequivalents of hydroxide were leached from the ash. Using the idea stated above, and calculating the amount of alkalinity which will be made available from the species analyzed, 18.1 milliequivalents of hydroxide were leached. This value is 10.6% below the figure obtained from the graph. Figure 4-1 indicates that 1.10 meq OH^-/g fly ash or 15.4 milliequivalents of hydroxide were leached at pH 8.5. Calculating the amount of alkalinity from the analyses of the leachate, 14.1 milliequivalents of alkalinity were leached. The alkalinity calculated from the analyses is 4.4% less than the value obtained from the graph. These values indicate that additional alkalinity in forms other than the oxides of calcium, magnesium, sodium, or potassium is present in the ash of Comanche Steam-Electric Station. Another possibility is that sulfate could be more available to the system in some form other than calcium sulfate or as a salt of one of the species listed above.

4.4.1.2 Plant Bowen

Calcium and sulfate are the major constituents leached from Plant Bowen coal ash. Magnesium, sodium, and potassium are much less concentrated in the ash. There is a significant difference in the sulfate to calcium ratio among the different pH values at which the ash was leached. The sulfate to calcium ratio at pH 6.0 is 0.413, but this ratio increased to 0.649 at pH 8.5, and to 0.734 at pH 10.4. It follows from these values that at a low pH value there is a tendency for more calcium in the form of CaO to be leached than $CaSO_4$ which is the other major form of calcium found in the fly ash. However, at higher pH values, less alkalinity was leached and $CaSO_4$ was the major form by which calcium was dissolved into the system. The sulfate being dissolved into the system was a result chiefly of $CaSO_4$ dissolution since magnesium, sodium and potassium are present in much smaller quantities than calcium (see Table 4-4).

Plant Bowen ash has available alkalinity of 0.43 meq OH^-/g ash as derived from the plot of meq acid/g fly ash versus time. At pH 6.0, 6.03 milliequivalents of hydroxide were leached during the experiment; 6.1 milliequivalents of hydroxide were calculated to have been leached, arriving in the form of the

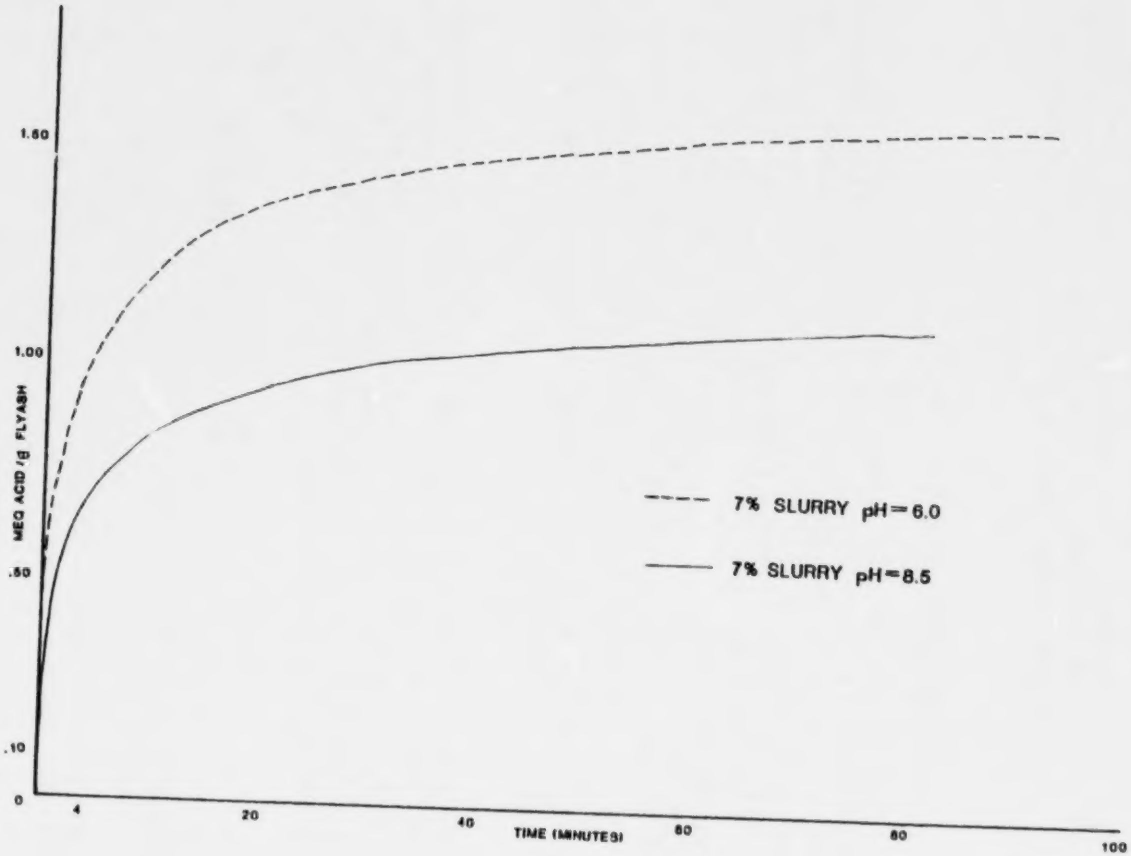

Figure 4-1. Comanche steam-electric station meq acid/g fly ash versus time.

oxides of calcium, magnesium, sodium and potassium using the analyses of the leachate. At pH 8.5, 0.14 meq OH^-/g fly ash and 1.95 milliequivalents of hydroxide leached were the values obtained from Figure 4-2; 2.2 milliequivalents of hydroxide were leached as calculated from the analyses of the leachate. No plot of meq acid/g fly ash versus time was made for the leaching study of Plant Bowen ash at pH 10.4 due to the low amount of alkalinity leached. The agreement between the values above indicates that the sulfate of the system is derived from $CaSO_4$ and that CaO is the major source of alkalinity found in Plant Bowen coal ash.

4.4.1.3 Four Corners Power Plant

Calcium is the single major constituent leached from coal ash of the Four Corners Power Plant. The sulfate leached is significant but well below the amount from the ashes of the two other plants as shown in Table 4-4. The amounts of magnesium, sodium and potassium leached were insignificant. Leaching a 7% slurry of the ash, the amounts of calcium and sulfate leached were more pronounced than that of a 2% slurry. However, the sulfate to calcium ratio from the 7% slurry was 0.077 at pH 3.0, 0.023 at pH 6.0, and 0.049 at pH 8.5. The sulfate to calcium ratios from the 2% slurries were insignificant. Leaching of the Four Corners Power Plant coal ash indicates that the available alkalinity is in the form of CaO, which is also the major form of calcium present in the ash.

The values of milliequivalents of hydroxide leached as CaO derived from the plots of meq acid/g fly ash versus time (Figures 4-3 and 4-4) agree well with the values obtained by calculating the hydroxide leached using the concentrations obtained by the analyses of the leachate for a 7% slurry. The corresponding values are as follows:

	pH 3.0	pH 6.0	pH 8.5
Calculated from analyses of leachate	5.52	5.00	4.28
Derived from meq acid/g fly ash versus time plots	5.85	5.32	4.25

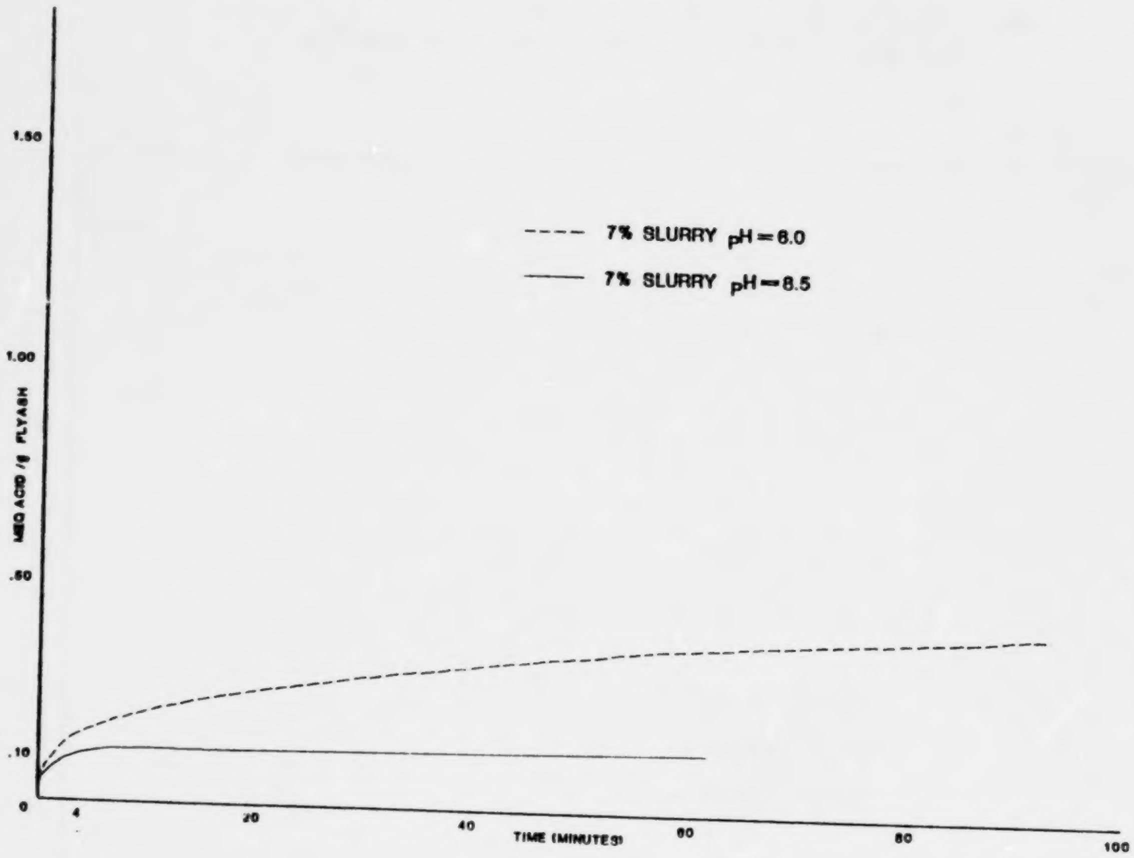

Figure 4-2. Plant Bowen meq acid/g fly ash versus time.

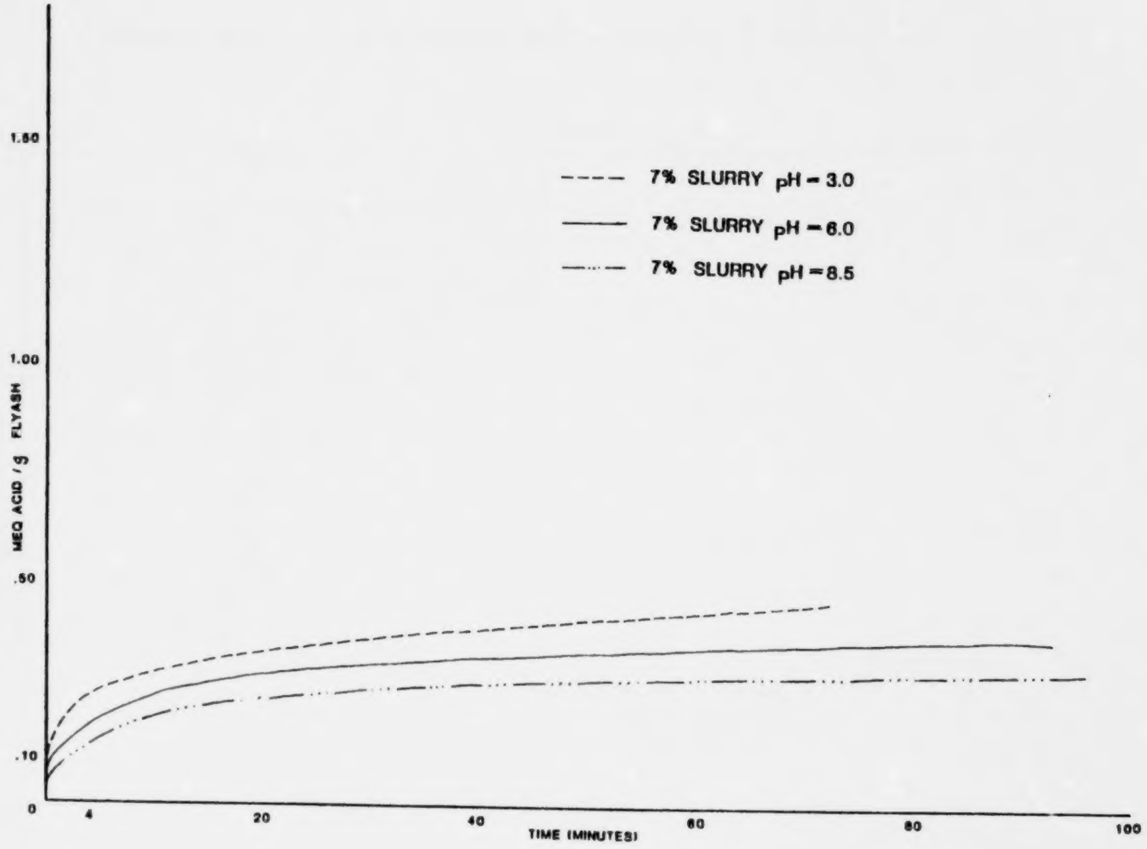

Figure 4-3. Four Corners power station meq acid/g fly ash versus time.

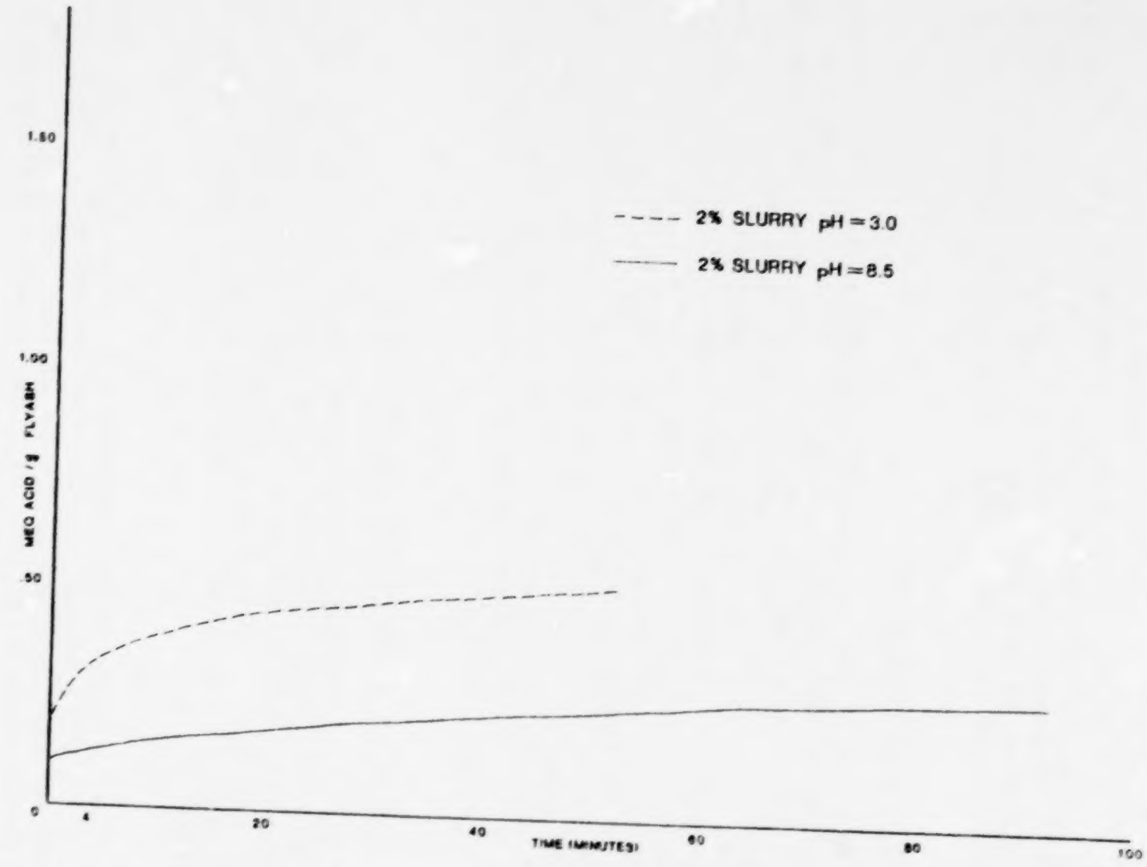

Figure 4-4. Four Corners power station
meq acid/g fly ash versus time.

These values show the agreement between the analyses of the leachate and Figure 4-3. There is little doubt that CaO is the major compound leached from Four Corners Power Plant as described by the analyses. The leaching performed with a 2% slurry also agreed well between the two methods of determining the alkalinity leached. At pH 3.0, 0.54 meq OH^-/g fly ash and 2.16 milliequivalents of hydroxide leached were derived from Figure 4-4; 1.77 milliequivalents of hydroxide were calculated from the analyses to have been leached. For pH 8.5, 1.18 milliequivalents of hydroxide was calculated to have been leached using the analyses values and 0.29 meq OH^-/g fly ash or 1.16 milliequivalents of hydroxide was derived from Figure 4-4.

4.4.2 Batch Dissolutions

The following section is a semiqualitative discussion of the results of the batch dissolution characterizations. These results are also compared to the closed-loop ash sluicing experimental results. It should be stated here that the ionic activities derived from the EMF values of the specific ion electrodes are significantly different from the ionic activities calculated by the chemical equilibrium computer program. The matrix to which the specific ion electrodes were subjected adversely affected the reliability of these electrodes. The liquor compositions were continuously changing, thereby changing the electrode calibration. Continuous calibration is not possible since the liquor composition changes are unknown when the experiment is being run. Results from the batch dissolution experiments were presented in Table 4-5.

4.4.2.1 Comanche Steam-Electric Station

The first batch dissolution characterization run with coal ash from Comanche Steam-Electric Station shows an increase in the concentration of calcium, the predominant species present, throughout the run. There was a final concentration of calcium of 6.18 mmole/ℓ. No other species had higher than 1 mmole/ℓ concentration.

The calcium concentration increased somewhat, from 3.09 mmolar to 6.73 mmolar during the second run. This increase is only 50% of the calcium increase of the first run. The chloride concentration doubled but no other species indicated a significant increase in concentration.

The third run, which was spiked with 0.417 mmole/ℓ carbonate and 5.21 mmole/ℓ sulfate, indicates calcium sulfate precipitation. The calcium concentration decreased by more than 50% from the initial quick dissolution of more than 2.5 mmole/ℓ and the sulfate concentration decreased by 4.5 mmole/ℓ. The carbonate concentration also decreased by one-half indicating calcium carbonate precipitation.

The fourth run had an initial sulfate concentration of 26.0 mmole/ℓ. This concentration was reduced to 18.1 mmole/ℓ while the calcium concentration was less than 1 mmole/ℓ after 30 minutes. At 10 minutes, the calcium concentration was 4 mmole/ℓ, due probably to the quick dissolution of calcium oxide. The carbonate concentration was reduced to slightly more than 0.2 mmole/ℓ which is approximately the final concentration of carbonate of each of the runs.

The fifth run also had a decrease in the calcium concentration, but a change of less than one mmole/ℓ. The sulfate concentration also decreased by less than one mmole/ℓ. The solution had a carbonate concentration initially of 1.67 mmole/ℓ, and, finally, as in the previous runs, 0.2 mmole/ℓ.

The information gathered from the last three runs indicates that calcium carbonate was precipitated. Calcium carbonate was supersaturated in the final liquors of each run. The reduction in the carbonate concentration which correlates to the calcium carbonate precipitation would not explain the amount of the decrease of the calcium concentration after the initial dissolution of calcium. The sulfate concentration had also decreased significantly in these runs. However, computer chemical equilibrium relative saturation values do not indicate calcium sulfate supersaturation which is necessary for precipitation of calcium sulfate. Also, the resulting liquor is below a relative saturation of one with respect to calcium hydroxide.

One possible explanation for this observation is that with a sluice liquor high in sulfate, the initial quick dissolution of CaO causes gypsum nucleation and precipitation to near saturation. Then, as calcium carbonate precipitates, the calcium concentration is lowered resulting in a subsaturated gypsum solution at the end of the run.

Magnesium hydroxide was supersaturated in the liquors of all the runs due to the high pH values. The concentrations of the species analyzed were well below the concentration values obtained from the ash dissolution characterizations. However, the pH values were very similar.

4.4.2.2 Plant Bowen

All five of the batch dissolution characterization experiments for Bowen ash exhibited almost the same characteristics. In each instance, approximately 10 mmole/ℓ of calcium, 10 mmole/ℓ sulfate, 1 mmole/ℓ sodium, and less than 1 mmole/ℓ chloride were dissolved into the liquor. Magnesium dissolution was quite low. The carbonate concentrations of the last three runs were reduced by calcium carbonate precipitation. Calcium carbonate was supersaturated in each of the liquors of the experiments as calculated by the chemical equilibrium program (relative saturations ranged from 13-26).

As compared to the ash dissolution characterizations, the batch dissolution characterizations exhibited lower calcium and sulfate concentrations. The pH of each of the runs using fly ash from Plant Bowen was lower than the pH observed during the ash dissolution characterizations of Plant Bowen fly ash.

4.4.2.3 Four Corners Power Plant

All five runs with fly ash from the Four Corners Power Plant exhibited an increase in the calcium concentrations with an upper limit of slightly more than 5 mmoles/ℓ. The sulfate, sodium, and chloride concentrations increased, although not substantially. Calcium carbonate precipitation probably occurred during the final three runs, being indicated by a decrease in carbonate concentration and supersaturation of calcium carbonate.

Even though magnesium concentrations were very low, the liquors of each run were supersaturated with magnesium hydroxide due to the high hydroxide concentrations.

The calcium concentrations of the batch dissolution characterizations were in the same range as the calcium concentrations of the ash dissolution characterizations. Other species analyzed from the batch dissolution characterizations were not as concentrated as in the ash dissolution characterizations. The pH values observed during the batch dissolution characterizations were more than one pH unit higher than the pH values observed during the ash dissolution characterizations.

APPENDIX LA

TEST PARAMETERS AND CHEMICAL ANALYSES FOR CLOSED-LOOP SLUICING TESTS

TABLE A-1. COMANCHE STEAM-ELECTRIC STATION RUN NO. 1

	Settling Pond		Mixing Tank[2]		Sluice Line	
	31 Hrs.	26 Hrs.	31 Hrs.	26 Hrs.	31 Hrs.[3]	26 Hrs.[3]
[1]Calcium	4.30	4.92	5.52	5.85	4.96	5.21
[1]Magnesium	.002	.002	.002	.004	.002	.002
[1]Sodium	6.36	4.45	7.22	6.04	7.12	5.72
[1]Sulfate	.49	.75	.20	.24	.17	.08
[1]Chloride	.675	.559	.805	.656	.705	.625
[1]Carbonate	.43	2.44	.29	.42	.18	.40
pH	11.9	11.7	11.9	11.1	11.8	11.5
T°C	21	19.5	23	21	---	---
a_{Ca}	7.9×10^{-4}	1.52×10^{-3}	1.1×10^{-3}	1.28×10^{-3}	9.3×10^{-4}	1.8×10^{-3}
a_{Mg}	1.4×10^{-3}	2.04×10^{-3}	1.1×10^{-3}	1.75×10^{-3}	1.1×10^{-3}	8.0×10^{-4}
a_{Ca}[4]	2.22×10^{-3}	1.99×10^{-3}	2.83×10^{-3}	3.34×10^{-3}	2.71×10^{-3}	2.95×10^{-3}
a_{Mg}[4]	4.72×10^{-7}	4.89×10^{-7}	4.24×10^{-7}	1.88×10^{-6}	5.25×10^{-7}	7.18×10^{-7}

Feed Rates to Mixing Tank:

Sluice water	710 ml/min.
Makeup water	40 ml/min.
Coal ash	56 g/min.

Makeup Water Composition:

Calcium	5.1	mmole/ℓ
Magnesium	2.7	mmole/ℓ
Sodium	6.3	mmole/ℓ
Sulfate	10.1	mmole/ℓ
Carbonate	.04	mmole/ℓ
Chloride	1.4	mmole/ℓ
Nitrate	.25	mmole/ℓ
pH	8.9	

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[1] Concentration in mmole/ℓ.

[2] Residence time of mixing tank is 6.4 minutes.

[3] Residence time of sluice line is 10 minutes.

[4] Ionic activities calculated by chemical equilibrium computer program.

TABLE A-2. COMANCHE STEAM-ELECTRIC STATION RUN NO. 2

	Settling Pond		Mixing Tank[2]		Sluice Line		
	48 Hrs.	43 Hrs.	48 Hrs.	43 Hrs.	48 Hrs.[3]	48 Hrs.[4]	43 Hrs.[3]
[1]Calcium	6.32	6.95	7.18	7.93	7.39	7.07	7.32
[1]Magnesium	.016	.017	.004	.009	.016	.028	.007
[1]Sodium	18.8	18.2	20.5	19.4	20.5	21.0	20.6
[1]Sulfate	7.84	7.82	7.78	8.61	8.58	8.69	8.81
[1]Chloride	1.12	1.01	1.09	1.03	1.11	1.15	1.06
[1]Carbonate	.31	.70	.18	.47	.15	.27	---
pH	11.9	12.0	12.15	11.9	12.0	12.0	11.6
T°C	23	23	24	23.5	---	---	---
a_{Ca}	$2.50\mathrm{x}10^{-4}$	$2.20\mathrm{x}10^{-5}$	$6.7\ \mathrm{x}10^{-4}$	$4.75\mathrm{x}10^{-5}$	$9.3\ \mathrm{x}10^{-4}$	$9.3\ \mathrm{x}10^{-4}$	$1.42\mathrm{x}10^{-4}$
a_{Mg}	$3.08\mathrm{x}10^{-3}$	$3.1\ \mathrm{x}10^{-3}$	$2.66\mathrm{x}10^{-3}$	$2.83\mathrm{x}10^{-3}$	$2.15\mathrm{x}10^{-3}$	$1.92\mathrm{x}10^{-3}$	$2.15\mathrm{x}10^{-3}$
a_{Ca}[5]	$2.25\mathrm{x}10^{-3}$	$2.34\mathrm{x}10^{-3}$	$2.38\mathrm{x}10^{-3}$	$2.72\mathrm{x}10^{-3}$	$2.54\mathrm{x}10^{-3}$	$2.40\mathrm{x}10^{-3}$	$2.62\mathrm{x}10^{-3}$
a_{Mg}[5]	$2.86\mathrm{x}10^{-6}$	$2.60\mathrm{x}10^{-6}$	$4.68\mathrm{x}10^{-7}$	$1.54\mathrm{x}10^{-6}$	$2.49\mathrm{x}10^{-6}$	$4.32\mathrm{x}10^{-6}$	$1.69\mathrm{x}10^{-6}$

Feed Rates to Mixing Tank:

Sluice water	710 ml/min
Makeup water	40 ml/min
Coal ash	56 g/min

Makeup Water Composition:

Calcium	5.1	mmole/ℓ
Magnesium	2.7	mmole/ℓ
Sodium	24.9	mmole/ℓ
Potassium	1.7	mmole/ℓ
Sulfate	20.2	mmole/ℓ
Carbonate	.04	mmole/ℓ
Chloride	1.4	mmole/ℓ
Nitrate	.3	mmole/ℓ
pH	9.2	

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[1] Concentration in mmole/ℓ.

[2] Residence time of mixing tank is 6.4 minutes.

[3] Residence time of sluice line is 10 minutes.

[4] Residence time of sluice line is 5 minutes.

[5] Ionic activities calculated by chemical equilibrium computer program.

TABLE A-3. COMANCHE STEAM-ELECTRIC STATION RUN NO. 3[1]

	Settling Pond		Mixing Tank[3]		Sluice Line		
	49 Hrs.	44 Hrs.	49 Hrs.	44 Hrs.	49 Hrs.[4]	49 Hrs.[5]	44 Hrs.[4]
[2]Calcium	7.68	8.68	8.49	8.46	8.07	7.39	8.41
[2]Magnesium	.005	.008	.006	.004	.006	.006	.006
[2]Sodium	18.4	13.8	14.4	13.0	15.2	15.0	13.4
[2]Sulfate	6.78	6.51	5.98	6.66	6.67	7.24	6.59
[2]Chloride	1.24	1.18	1.25	1.23	1.22	1.24	1.20
[2]Carbonate	.26	.25	.12	.14	.21	.11	.15
pH	12.2	12.0	12.2	12.1	12.2	12.2	12.2
T°C	21	21	23	23	24.5	24.5	23
a_{Ca}	---	7.9×10^{-4}	---	9.6×10^{-4}	---	---	2.37×10^{-3}
a_{Mg}	---	9.1×10^{-3}	---	3.2×10^{-3}	---	---	2.1×10^{-3}
a_{Ca}[6]	2.69×10^{-3}	3.27×10^{-3}	3.01×10^{-3}	3.04×10^{-3}	2.71×10^{-3}	2.46×10^{-3}	2.92×10^{-3}
a_{Mg}[6]	6.63×10^{-7}	1.44×10^{-6}	7.08×10^{-7}	5.53×10^{-7}	6.32×10^{-7}	6.31×10^{-7}	7.04×10^{-7}

Feed Rates to Mixing Tank:

Sluice water	710 ml/min
Makeup water	40 ml/min
Coal ash	56 g/min

Makeup Water Composition:

Calcium	5.1 mmole/ℓ
Magnesium	2.7 mmole/ℓ
Sodium	6.3 mmole/ℓ
Sulfate	10.1 mmole/ℓ
Carbonate	.04 mmole/ℓ
Chloride	1.4 mmole/ℓ
Nitrate	.25 mmole/ℓ
pH	8.9

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[1] Fan positioned to blow across surface of settling pond.

[2] Concentration in mmole/ℓ.

[3] Residence time of mixing tank is 6.4 minutes.

[4] Residence time of sluice line is 10 minutes.

[5] Residence time of sluice line is 5 minutes.

[6] Ionic activities calculated by chemical equilibrium computer program.

TABLE A-4. COMANCHE STEAM-ELECTRIC STATION RUN NO. 4

	Settling Pond		Mixing Tank[2]		Sluice Line		
	50 Hrs.	45 Hrs.	50 Hrs.	45 Hrs.	50 Hrs.[3]	50 Hrs.[4]	45 Hrs.[3]
[1]Calcium	8.98	9.04	10.4	10.7	9.97	9.76	9.68
[1]Magnesium	.004	.007	.006	.004	.012	.008	.013
[1]Sodium	14.1	9.63	10.3	10.1	17.8	16.0	8.50
[1]Sulfate	6.26	5.50	7.63	6.94	6.93	6.80	6.40
[1]Chloride	1.18	1.28	1.20	1.24	1.24	1.25	1.20
[1]Carbonate	.058	.122	.063	.072	.080	.170	.122
pH	11.95	12.0	11.9	11.9	11.95	11.95	11.95
T°C	22	22	23	23	23	23	22.5
a_{Ca}	2.20×10^{-3}	1.27×10^{-3}	2.55×10^{-3}	1.73×10^{-3}	1.22×10^{-3}	2.04×10^{-3}	7.25×10^{-4}
a_{Mg}	1.40×10^{-3}	2.56×10^{-3}	1.66×10^{-3}	2.44×10^{-3}	2.67×10^{-3}	2.17×10^{-3}	2.84×10^{-3}
a_{Ca}[5]	3.46×10^{-3}	3.55×10^{-3}	3.86×10^{-3}	4.06×10^{-3}	3.68×10^{-3}	3.61×10^{-3}	3.72×10^{-3}
a_{Mg}[5]	7.38×10^{-7}	1.22×10^{-6}	1.10×10^{-6}	7.41×10^{-7}	2.06×10^{-6}	1.37×10^{-6}	2.33×10^{-6}

Feed Rates to Mixing Tank:

Sluice water	710 ml/min
Makeup water	40 ml/min
Coal ash	56 g/min

Makeup Water Composition:

Calcium	5.1 mmole/ℓ
Magnesium	2.7 mmole/ℓ
Sodium	6.3 mmole/ℓ
Sulfate	10.1 mmole/ℓ
Carbonate	.04 mmole/ℓ
Chloride	1.4 mmole/ℓ
Nitrate	.25 mmole/ℓ
pH	8.9

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[1] Concentration in mmole/ℓ.

[2] Residence time of mixing tank is 3.2 minutes.

[3] Residence time of sluice line is 10 minutes.

[4] Residence time of sluice line is 5 minutes.

[5] Ionic activities calculated by chemical equilibrium computer program.

TABLE A-5. COMANCHE STEAM-ELECTRIC STATION RUN NO. 5

	Settling Pond		Mixing Tank[2]		Sluice Line		
	50 Hrs.	45 Hrs.	50 Hrs.	45 Hrs.	50 Hrs.[3]	50 Hrs.[4]	45 Hrs.[3]
[1]Calcium	11.2	11.0	12.6	9.71	11.9	12.0	10.2
[1]Magnesium	.450	.849	.055	.594	.188	.103	.164
[1]Sodium	16.6	20.0	10.2	16.4	16.5	19.4	14.9
[1]Sulfate	12.6	11.4	13.4	12.3	14.0	13.6	12.1
[1]Chloride	1.20	1.21	1.26	1.18	1.26	1.24	1.20
[1]Carbonate	3.93	6.87	.150	.392	.210	.143	.263
pH	7.1	7.45	11.2	10.8	9.8	10.7	10.7
T°C	24	24	24	24	25	25	24
a_{Ca}	7.9×10^{-4}	1.05×10^{-3}	2.30×10^{-3}	2.52×10^{-3}	1.12×10^{-3}	2.90×10^{-3}	5.7×10^{-4}
a_{Mg}	2.4×10^{-3}	2.75×10^{-3}	1.52×10^{-3}	9.8×10^{-4}	2.16×10^{-3}	6.2×10^{-4}	2.63×10^{-3}
a_{Ca}[5]	3.79×10^{-3}	3.74×10^{-3}	4.22×10^{-3}	3.46×10^{-3}	3.94×10^{-3}	3.99×10^{-3}	3.51×10^{-3}
a_{Mg}[5]	1.64×10^{-4}	3.12×10^{-4}	8.70×10^{-5}	1.94×10^{-4}	6.58×10^{-5}	3.39×10^{-5}	5.56×10^{-5}

Feed Rates to Mixing Tank:

Sluice water	710 ml/min
Makeup water	40 ml/min
Coal ash	56 g/min

Makeup Water Composition:

Calcium	5.1	mmole/ℓ
Magnesium	2.7	mmole/ℓ
Sodium	6.3	mmole/ℓ
Sulfate	10.1	mmole/ℓ
Carbonate	.04	mmole/ℓ
Chloride	1.4	mmole/ℓ
Nitrate	.25	mmole/ℓ
pH	8.9	

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[1] Concentration in mmole/ℓ.

[2] Residence time of mixing tank is 3.2 minutes.

[3] Residence time of sluice line is 10 minutes.

[4] Residence time of sluice line is 5 minutes.

[5] Ionic activities calculated by chemical equilibrium computer program.

TABLE A-6. PLANT BOWEN RUN NO. 1

	Settling Pond		Mixing Tank[2]		Sluice Line	
	48 Hrs.	43 Hrs.	48 Hrs.	43 Hrs.	48 Hrs.[3]	43 Hrs.[3]
[1]Calcium	16.4	16.0	22.8	22.4	22.9	23.0
[1]Magnesium	.014	.008	.010	.005	.014	.006
[1]Sodium	8.32	12.6	4.66	5.92	8.66	6.68
[1]Sulfate	10.3	9.95	12.7	12.6	12.8	12.5
[1]Chloride	1.26	1.32	1.25	1.23	1.28	1.29
[1]Carbonate	.281	.187	.292	.240	.155	.213
pH	11.9	11.85	12.1	12.05	12.1	12.0
T°C	23	23	23.5	23.5	25	24
a_{Ca}	$2.87x10^{-3}$	$9.9\ x10^{-4}$	$3.13x10^{-3}$	$7.9\ x10^{-4}$	$4.07x10^{-3}$	$4.16x10^{-3}$
a_{Mg}	$2.9\ x10^{-3}$	$5.2\ x10^{-3}$	$5.4\ x10^{-3}$	$7.7\ x10^{-3}$	$5.2\ x10^{-3}$	$3.6\ x10^{-3}$
a_{Ca}[4]	$5.59x10^{-3}$	$5.54x10^{-3}$	$7.00x10^{-3}$	$6.99x10^{-3}$	$6.89x10^{-3}$	$7.24x10^{-3}$
a_{Mg}[4]	$2.44x10^{-6}$	$1.49x10^{-6}$	$1.25x10^{-6}$	$6.73x10^{-7}$	$1.59x10^{-6}$	$8.44x10^{-7}$

Feed Rates to Mixing Tank:

Sluice water	710 ml/min
Makeup water	40 ml/min
Coal ash	56 g/min

Makeup Water Composition:

Calcium	5.1 mmole/ℓ
Magnesium	2.7 mmole/ℓ
Sodium	6.3 mmole/ℓ
Sulfate	10.1 mmole/ℓ
Carbonate	.04 mmole/ℓ
Chloride	1.4 mmole/ℓ
Nitrate	.25 mmole/ℓ
pH	8.9

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[1] Concentration in mmole/ℓ.

[2] Residence time of mixing tank is 6.4 minutes.

[3] Residence time of sluice line is 10 minutes.

[4] Ionic activities calculated by chemical equilibrium computer program.

TABLE A-7. PLANT BOWEN RUN NO. 2

	Settling Pond		Mixing Tank[2]		Sluice Line		
	50 Hrs.	45 Hrs.	50 Hrs.	45 Hrs.	50 Hrs.[3]	50 Hrs.[4]	45 Hrs.[3]
[1]Calcium	20.7	19.6	23.0	22.0	22.5	21.8	21.4
[1]Magnesium	.020	.012	.102	.072	.090	.062	.074
[1]Sodium	15.6	12.3	15.2	14.1	14.5	15.9	14.5
[1]Sulfate	23.3	22.0	26.2	24.7	26.2	26.4	25.2
[1]Chloride	1.28	1.31	3.66	1.33	1.28	1.29	1.24
[1]Carbonate	.169	.109	--	.125	.119	.112	.147
pH	11.3	11.3	10.6	11.1	10.85	11.0	10.75
T°C	20.5	19.5	22	21	22.5	22.5	21.5
a_{Ca}	2.02×10^{-3}	2.44×10^{-3}	1.17×10^{-3}	1.38×10^{-3}	1.17×10^{-3}	3.25×10^{-3}	3.6×10^{-3}
a_{Mg}	2.13×10^{-3}	1.96×10^{-3}	3.33×10^{-3}	3.02×10^{-3}	3.33×10^{-3}	9.0×10^{-4}	1.2×10^{-3}
a_{Ca}[5]	5.80×10^{-3}	5.64×10^{-3}	6.22×10^{-3}	6.08×10^{-3}	6.06×10^{-3}	5.82×10^{-3}	5.86×10^{-3}
a_{Mg}[5]	5.11×10^{-6}	3.18×10^{-6}	2.87×10^{-5}	1.92×10^{-5}	2.44×10^{-5}	1.62×10^{-5}	2.08×10^{-5}

Feed Rates to Mixing Tank:

Sluice water	710 ml/min
Makeup water	40 ml/min
Coal ash	56 g/min

Makeup Water Composition:

Calcium	5.1	mmole/ℓ
Magnesium	2.7	mmole/ℓ
Sodium	24.9	mmole/ℓ
Potassium	1.7	mmole/ℓ
Sulfate	20.2	mmole/ℓ
Carbonate	.04	mmole/ℓ
Chloride	1.4	mmole/ℓ
Nitrate	.3	mmole/ℓ
pH	9.2	

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[1] Concentration in mmole/ℓ.

[2] Residence time of mixing tank is 6.4 minutes.

[3] Residence time of sluice line is 10 minutes.

[4] Residence time of sluice line is 5 minutes.

[5] Ionic activities calculated by chemical equilibrium computer program.

TABLE A-8. PLANT BOWEN RUN NO. 3

	Settling Pond		Mixing Tank[2]		Sluice Line		
	48 Hrs.	43 Hrs.	48 Hrs.	43 Hrs.	48 Hrs.[3]	48 Hrs.[4]	43 Hrs.[3]
[1]Calcium	18.4	18.3	20.0	19.9	20.0	20.0	20.6
[1]Magnesium	.015	.012	.048	.048	.044	.035	.040
[1]Sodium	11.4	13.4	14.2	17.6	13.6	14.3	18.2
[1]Sulfate	21.0	20.6	21.9	22.1	22.0	22.1	22.2
[1]Chloride	.992	.983	.958	.977	.976	.949	.980
[1]Carbonate	.160	.091	.110	.092	.075	.147	.119
pH	11.3	11.3	11.1	11.1	11.05	11.2	11.2
T°C	24.5	24	25	25.5	26.5	26.5	25
a_{Ca}	3.6×10^{-3}	2.62×10^{-3}	1.9×10^{-3}	2.87×10^{-3}	3.9×10^{-3}	4.5×10^{-3}	1.43×10^{-3}
a_{Mg}	1.2×10^{-3}	3.1×10^{-3}	2.9×10^{-3}	2.8×10^{-3}	2.0×10^{-4}	3.0×10^{-4}	4.3×10^{-3}
a_{Ca}[5]	5.25×10^{-3}	5.28×10^{-3}	5.68×10^{-3}	5.61×10^{-3}	5.65×10^{-3}	5.59×10^{-3}	5.80×10^{-3}
a_{Mg}[5]	3.65×10^{-6}	2.98×10^{-6}	1.25×10^{-5}	1.24×10^{-5}	1.14×10^{-5}	8.48×10^{-6}	9.99×10^{-6}

Feed Rates to Mixing Tank:

Sluice water	710 ml/min
Makeup water	40 ml/min
Coal ash	56 g/min

Makeup Water Composition:

Calcium	.75 mmole/ℓ
Magnesium	.35 mmole/ℓ
Sodium	1.0 mmole/ℓ
Sulfate	.10 mmole/ℓ
Carbonate	1.71 mmole/ℓ
Chloride	.24 mmole/ℓ
pH	7.8

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[1] Concentration in mmole/ℓ.

[2] Residence time of mixing tank is 6.4 minutes.

[3] Residence time of sluice line is 10 minutes.

[4] Residence time of sluice line is 5 minutes.

[5] Ionic activities calculated by chemical equilibrium computer program.

TABLE A-9. PLANT BOWEN RUN NO. 4

	Settling Pond[6]		Mixing Tank[2]		Sluice Line		
	47 Hrs.	42 Hrs.	47 Hrs.	42 Hrs.	47 Hrs.[3]	47 Hrs.[4]	42 Hrs.[3]
[1]Calcium	18.5	17.4	21.2	19.8	21.7	21.6	20.1
[1]Magnesium	.494	.450	.334	.475	.054	.392	.368
[1]Sodium	4.54	4.36	5.12	4.72	4.98	5.01	4.78
[1]Sulfate	18.5	17.3	20.8	19.7	20.8	21.3	19.8
[1]Chloride	1.33	1.37	1.38	1.34	1.34	1.34	1.38
[1]Carbonate	2.19	2.32	.333	.222	.210	.439	.205
pH	8.4	8.4	10.6	10.0	11.0	10.2	10.3
T°C	23	23	23	23	24	24.5	24
a_{Ca}	3.13×10^{-4}	1.83×10^{-4}	7.9×10^{-3}	4.7×10^{-3}	3.20×10^{-3}	2.90×10^{-3}	1.37×10^{-3}
a_{Mg}	4.5×10^{-3}	4.0×10^{-3}	--	1.0×10^{-3}	2.4×10^{-3}	2.4×10^{-3}	3.9×10^{-3}
a_{Ca}[5]	5.65×10^{-3}	5.43×10^{-3}	6.25×10^{-3}	6.00×10^{-3}	6.38×10^{-3}	6.28×10^{-3}	6.05×10^{-3}
a_{Mg}[5]	1.62×10^{-4}	1.51×10^{-4}	1.01×10^{-4}	1.52×10^{-4}	1.12×10^{-4}	1.20×10^{-4}	1.16×10^{-4}

Feed Rates to Mixing Tank:

Sluice water	710 ml/min
Makeup water	40 ml/min
Coal ash	56 g/min

Makeup Water Composition:

Calcium	5.1 mmole/ℓ
Magnesium	2.7 mmole/ℓ
Sodium	6.3 mmole/ℓ
Sulfate	10.1 mmole/ℓ
Carbonate	.04 mmole/ℓ
Chloride	1.4 mmole/ℓ
Nitrate	.25 mmole/ℓ
pH	8.9

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[1] Concentration in mmole/ℓ.

[2] Residence time of mixing tank is 3.2 minutes.

[3] Residence time of sluice line is 10 minutes.

[4] Residence time of sluice line is 5 minutes.

[5] Ionic activities calculated by chemical equilibrium computer program.

[6] Carbon dioxide bubbled through settling pond at the rate of 0.5 ℓ/min.

TABLE A-10. FOUR CORNERS POWER PLANT RUN NO. 1

	Settling Pond		Mixing Tank[2]		Sluice Line		
	46 Hrs.	41 Hrs.	46 Hrs.	41 Hrs.	46 Hrs.[3]	46 Hrs.[4]	41 Hrs.[3]
[1]Calcium	2.51	1.93	2.64	2.26	2.60	2.60	2.12
[1]Magnesium	.207	.232	.259	.259	.223	.187	.207
[1]Sodium	8.05	12.8	7.62	8.14	13.6	2.93	2.17
[1]Sulfate	2.40	2.36	2.81	2.74	2.94	2.93	2.17
[1]Chloride	1.47	1.42	1.44	1.48	1.46	1.40	1.42
[1]Carbonate	.506	.369	.372	.420	.246	.375	.410
pH	10.55	10.4	10.5	10.4	10.55	10.6	10.45
T°C	22	22	23	23	24	24	24
a_{Ca}	2.9×10^{-4}	5.35×10^{-4}	7.0×10^{-5}	4.26×10^{-4}	1.9×10^{-4}	4.7×10^{-4}	6.23×10^{-4}
a_{Mg}	5.0×10^{-4}	3.2×10^{-4}	7.8×10^{-4}	6.3×10^{-4}	7.5×10^{-4}	4.7×10^{-4}	3.2×10^{-4}
a_{Ca}[5]	1.26×10^{-3}	9.83×10^{-4}	1.32×10^{-3}	1.13×10^{-3}	1.28×10^{-3}	1.30×10^{-3}	1.12×10^{-3}
a_{Mg}[5]	9.72×10^{-5}	1.14×10^{-4}	1.23×10^{-4}	1.24×10^{-4}	1.05×10^{-4}	8.68×10^{-5}	1.02×10^{-4}

Feed Rates to Mixing Tank:

Sluice water	710 ml/min
Makeup water	40 ml/min
Coal ash	56 g/min

Makeup Water Composition:

Calcium	5.1 mmole/ℓ
Magnesium	2.7 mmole/ℓ
Sodium	6.3 mmole/ℓ
Sulfate	10.1 mmole/ℓ
Carbonate	.04 mmole/ℓ
Chloride	1.4 mmole/ℓ
Nitrate	.25 mmole/ℓ
pH	8.9

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[1] Concentration in mmole/ℓ.

[2] Residence time of mixing tank is 6.4 minutes.

[3] Residence time of sluice line is 10 minutes.

[4] Residence time of sluice line is 5 minutes.

[5] Ionic act'vities calculated by chemical equilibrium computer program.

TABLE A-11. FOUR CORNERS POWER PLANT RUN NO. 2

	Settling Pond		Mixing Tank[2]		Sluice Line		
	46 Hrs.	41 Hrs.	46 Hrs.	41 Hrs.	46 Hrs.[3]	46 Hrs.[4]	41 Hrs.[3]
[1]Calcium	5.06	5.19	6.16	5.90	5.78	5.62	5.58
[1]Magnesium	.170	.174	.189	.196	.150	.216	.172
[1]Sodium	10.4	11.1	12.6	10.8	14.1	10.8	12.0
[1]Sulfate	6.72	6.40	7.24	7.18	7.58	7.54	7.19
[1]Chloride	2.19	2.07	2.32	2.24	2.28	2.34	2.24
[1]Carbonate	.458	.655	.379	.633	.342	.439	.423
pH	10.6	10.6	10.6	10.6	10.55	10.4	10.6
T°C	19	19	21	20	22.5	22.5	21.5
a_{Ca}	1.15×10^{-3}	1.74×10^{-3}	7.9×10^{-4}	1.24×10^{-3}	1.24×10^{-3}	1.56×10^{-3}	1.33×10^{-3}
a_{Mg}	8.7×10^{-4}	4.6×10^{-4}	1.4×10^{-3}	3.6×10^{-4}	1.13×10^{-3}	6.3×10^{-4}	8.7×10^{-4}
a_{Ca}[5]	2.06×10^{-3}	2.10×10^{-3}	2.46×10^{-3}	2.32×10^{-3}	2.27×10^{-3}	2.21×10^{-3}	2.22×10^{-3}
a_{Mg}[5]	6.80×10^{-5}	6.84×10^{-5}	7.44×10^{-5}	7.52×10^{-5}	5.82×10^{-5}	8.45×10^{-5}	6.70×10^{-5}

Feed Rates to Mixing Tank:

Sluice water	710 ml/min
Makeup water	40 ml/min
Coal ash	56 g/min

Makeup Water Composition:

Calcium	16	mmole/ℓ
Magnesium	1.8	mmole/ℓ
Sodium	13	mmole/ℓ
Potassium	.3	mmole/ℓ
Sulfate	21.3	mmole/ℓ
Carbonate	.5	mmole/ℓ
Chloride	5	mmole/ℓ
Nitrate	.3	mmole/ℓ
pH	9.1	

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[1] Concentration in mmole/ℓ.

[2] Residence time of mixing tank is 6.4 minutes.

[3] Residence time of sluice line is 10 minutes.

[4] Residence time of sluice line is 5 minutes.

[5] Ionic activities calculated by chemical equilibrium computer program.

TABLE A-12. FOUR CORNERS POWER PLANT RUN NO. 3

	Settling Pond[6]		Mixing Tank[2]		Sluice Line		
	50 Hrs.	45 Hrs.	50 Hrs.	45 Hrs.	50 Hrs.[3]	50 Hrs.[4]	45 Hrs.[3]
[1]Calcium	3.40	3.88	3.34	3.27	3.50	3.08	3.43
[1]Magnesium	.739	.736	.744	.750	.740	.704	.734
[1]Sodium	4.48	4.92	4.93	4.76	4.98	5.03	5.12
[1]Sulfate	4.00	3.80	4.20	4.10	4.30	4.40	4.10
[1]Chloride	1.38	1.40	1.30	1.30	1.37	1.36	1.38
[1]Carbonate	2.92	2.99	2.61	2.60	2.32	2.03	2.41
pH	8.2	8.2	8.7	8.7	8.7	8.9	8.7
T°C	23	23	23	22	23	23	23
a_{Ca}	6.5×10^{-3}	1.05×10^{-3}	2.80×10^{-3}	9.7×10^{-4}	3.43×10^{-3}	7.2×10^{-3}	1.21×10^{-3}
a_{Mg}	---	9.7×10^{-4}	1.7×10^{-3}	9.0×10^{-4}	---	---	6.6×10^{-4}
a_{Ca}[5]	1.61×10^{-3}	1.85×10^{-3}	1.54×10^{-3}	1.52×10^{-3}	1.61×10^{-3}	1.40×10^{-3}	1.59×10^{-3}
a_{Mg}[5]	3.65×10^{-4}	3.66×10^{-4}	3.52×10^{-4}	3.58×10^{-4}	3.51×10^{-4}	3.28×10^{-3}	3.51×10^{-4}

Feed Rates to Mixing Tank:

Sluice water	710 ml/min
Makeup water	40 ml/min
Coal ash	56 g/min

Makeup Water Composition:

Calcium	5.1 mmole/ℓ
Magnesium	2.7 mmole/ℓ
Sodium	6.3 mmole/ℓ
Sulfate	10.1 mmole/ℓ
Carbonate	.04 mmole/ℓ
Chloride	1.4 mmole/ℓ
Nitrate	.25 mmole/ℓ
pH	8.9

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[1] Concentration in mmole/ℓ.

[2] Residence time of mixing tank is 3.2 minutes.

[3] Residence time of sluice line is 10 minutes.

[4] Residence time of sluice line is 5 minutes.

[5] Ionic activities calculated by chemical equilibrium computer program.

[6] Carbon dioxide bubbled through settling pond at the rate of 0.5 ℓ/min.

APPENDIX LB

CORRELATION PARAMETERS FOR CLOSED-LOOP SLUICING TESTS

Appendix LB contains the information which was used to determine if the ash dissolution characterization experiments were sampled at steady-state. The information which was used to derive the graphs which illustrate the dissolution occuring in the mix tank of the bench-scale model of a closed-loop ash sluicing facility also appears in Appendix LB.

Tables B-1, B-2, and B-3 contain calcium concentrations of samples which were taken throughout the ash dissolution characterization experiments. The calcium concentrations contained in these tables were used to determine if the final samples were collected after the system had achieved steady-state.

Tables B-4 and B-5 contain the information which was used to depict the dissolution of fly ash from Comanche Steam-Electric Station and Plant Bowen. The tables contain the dissolution rates of various species and related ionic activities and activity products which were used to characterize the dissolution of the fly ash of the respective plants. Although the same information was provided for Four Corners Power Plant ash dissolution (Table B-6), the data did not provide a sufficient range over which the data could be plotted. Therefore, possibly erroneous graphs could be drawn. For this reason, illustration of the dissolution of Four Corners Power Plant fly ash was considered inappropriate.

TABLE B-1. CALCIUM CONCENTRATIONS OF SAMPLED STREAMS DURING BENCH-SCALE EXPERIMENTS FOR COMANCHE[1]

	Time (Hours)	Settling Pond	Mixing Tank	Sluice Line
Run No. 1	5	5.25	6.96	6.77
	10	5.32	6.84	5.44
	15	5.41	6.39	5.21
	21	4.98	5.57	4.54
	26	4.92	5.85	5.21
	31	4.30	5.52	4.96
Run No. 2	8	4.62	4.32	5.59
	14	4.19	6.24	5.71
	18	4.39	6.69	6.49
	23	5.99	7.98	7.73
	39	5.86	8.03	7.36
	43	6.95	7.93	7.32
	48	6.32	7.18	7.39
Run No. 3	6	5.09	6.70	5.58
	12	5.81	6.86	6.07
	19	6.68	8.64	8.17
	26	6.70	8.38	7.75
	35	7.75	8.83	8.87
	44	8.68	8.46	8.41
	49	7.68	8.49	8.07
Run No. 4	17	5.36	7.16	6.43
	26	5.65	6.23	8.19
	33	7.40	9.20	8.14
	40	8.26	9.90	9.16
	45	9.04	10.7	9.68
	50	8.98	10.4	9.97
Run No. 5	17	8.87	7.43	7.97
	24	7.74	10.9	8.19
	40	9.49	9.73	--
	45	11.0	9.71	10.2
	50	11.2	12.6	11.9

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[1] Concentrations in mmole/ℓ.

TABLE B-2. CALCIUM CONCENTRATIONS OF SAMPLED STREAMS DURING ASH DISSOLUTION CHARACTERIZATION OF PLANT BOWEN COAL ASH[1]

	Time (Hours)	Settling Pond	Mixing Tank	Sluice Line
Run No. 1	15	6.29	11.7	10.5
	24	10.0	15.7	16.4
	30	12.7	19.3	18.2
	39	13.9	16.6	16.4
	43	16.0	22.4	23.0
	48	16.4	22.8	22.9
Run No. 2	10	15.5	16.3	16.4
	18	--	17.9	17.5
	26	16.7	19.1	18.6
	40	18.5	20.7	20.4
	45	19.6	22.0	21.4
	50	20.7	23.0	22.5
Run No. 3	12	17.2	17.8	18.9
	20	16.9	19.6	19.6
	28	18.3	19.4	20.0
	36	18.0	19.3	19.3
	43	18.3	19.9	20.6
	48	18.4	20.0	20.0
Run No. 4	15	9.35	12.5	12.7
	22	11.5	14.5	14.9
	38	17.9	16.4	17.8
	42	17.4	19.8	20.1
	47	18.5	21.2	21.7

[1] Concentrations in mmole/ℓ.

TABLE B-3. CALCIUM CONCENTRATIONS OF SAMPLED STREAMS DURING ASH DISSOLUTION CHARACTERIZATION OF FOUR CORNERS POWER PLANT COAL ASH[1]

	Time (Hours)	Settling Pond	Mixing Tank	Sluice Line
Run No. 1	15	1.14	1.21	1.41
	24	1.28	1.57	1.58
	31	1.58	1.73	1.85
	36	1.66	2.00	2.22
	41	1.93	2.26	2.12
	46	2.51	2.64	2.60
Run No. 2	13	2.66	3.28	3.08
	27	3.10	3.95	4.03
	36	4.71	4.69	4.60
	41	5.19	5.90	5.58
	46	5.06	6.16	5.78
Run No. 3	5	1.72	2.25	2.25
	30	3.40	3.08	2.93
	38	3.42	3.27	3.34
	45	3.88	3.27	3.43
	50	3.40	3.34	3.50

[1] Concentrations in mmole/ℓ.

TABLE B-4. COMANCHE STEAM-ELECTRIC STATION DISSOLUTION AND PRECIPITATION RATES, IONIC ACTIVITIES AND ACTIVITY PRODUCTS IN MIX TANK

	Calcium Dissolution Mmole/min	Sulfate Dissolution Mmole/min	$CaCO_3$ Precipitation Mmole/min	a_{Ca}	a_{SO_4}	$a_{Ca}\ a_{SO_4}$	$a_{Ca}\ a_{CO_3}$
Run No. 1	.88	-.60	.089	2.83×10^{-3}	8.51×10^{-5}	2.41×10^{-7}	1.23×10^{-7}
Run No. 2	.69	-.54	.087	2.38×10^{-3}	2.78×10^{-3}	6.61×10^{-6}	5.78×10^{-8}
Run No. 3	.71	-.73	.097	3.01×10^{-3}	2.12×10^{-3}	6.37×10^{-6}	4.62×10^{-8}
Run No. 4	1.22	.87	-.004	3.86×10^{-3}	2.59×10^{-3}	9.98×10^{-6}	2.76×10^{-8}
Run No. 5	1.29	.70	2.68	4.22×10^{-3}	4.22×10^{-3}	1.78×10^{-5}	6.41×10^{-8}

TABLE B-5. PLANT BOWEN DISSOLUTION AND PRECIPITATION RATES, IONIC ACTIVITIES AND ACTIVITY PRODUCTS IN MIX TANK

	Calcium Dissolution Mmole/min	Sulfate Dissolution Mmole/min	$CaCO_3$ Precipitation Mmole/min	a_{Ca}	a_{SO_4}	$a_{Ca}\ a_{SO_4}$	$a_{Ca}\ a_{CO_3}$
Run No. 1	5.25	1.81	-.018	7.00×10^{-3}	3.23×10^{-3}	2.26×10^{-5}	1.51×10^{-7}
Run No. 2	2.35	2.30	-.015	6.22×10^{-3}	6.47×10^{-3}	4.02×10^{-5}	6.70×10^{-8}
Run No. 3	1.91	1.51	.100	5.68×10^{-3}	5.72×10^{-3}	3.24×10^{-5}	4.93×10^{-8}
Run No. 4	2.56	2.06	1.31	6.25×10^{-3}	5.47×10^{-3}	3.42×10^{-5}	1.56×10^{-7}

TABLE B-6. FOUR CORNERS POWER PLANT DISSOLUTION AND PRECIPITATION RATES, IONIC ACTIVITIES AND ACTIVITY PRODUCTS IN MIX TANK

	Calcium Dissolution Mmole/min	Sulfate Dissolution Mmole/min	$CaCO_3$ Precipitation Mmole/min	a_{Ca}	a_{SO_4}	$a_{Ca}\ a_{SO_4}$	$a_{Ca}\ a_{CO_3}$
Run No. 1	0.0	.01	.082	1.32×10^{-3}	1.42×10^{-3}	1.88×10^{-6}	9.16×10^{-8}
Run No. 2	.39	-.19	.061	2.46×10^{-3}	2.87×10^{-3}	7.06×10^{-6}	1.25×10^{-7}
Run No. 3	-.10	-.09	.117	1.54×10^{-3}	1.98×10^{-3}	3.04×10^{-6}	6.94×10^{-8}

APPENDIX LC

pH AND EMF VALUES OF CALCIUM AND DIVALENT CATION SPECIFIC ELECTRODES FOR BATCH DISSOLUTION TESTS

Appendix LC contains the charts obtained by instrumentally monitoring pH and EMF values of calcium and divalent cation specific ion electrodes from the experiments conducted during the batch dissolution characterizations. The tests were performed upon coal ash from three coal-fired electric generating plants.

1) Comanche Steam-Electric Plant of Public Service Company of Colorado,

2) Four Corners Power Plant of Arizona Public Services, and

3) Plant Bowen of Georgia Power Company.

Experiments were conducted upon a 7% slurry of fly ash from each of the plants and liquors of varying chemical compositions.

Each fly ash was subjected to five various chemical compositions which are identified by run number as follows:

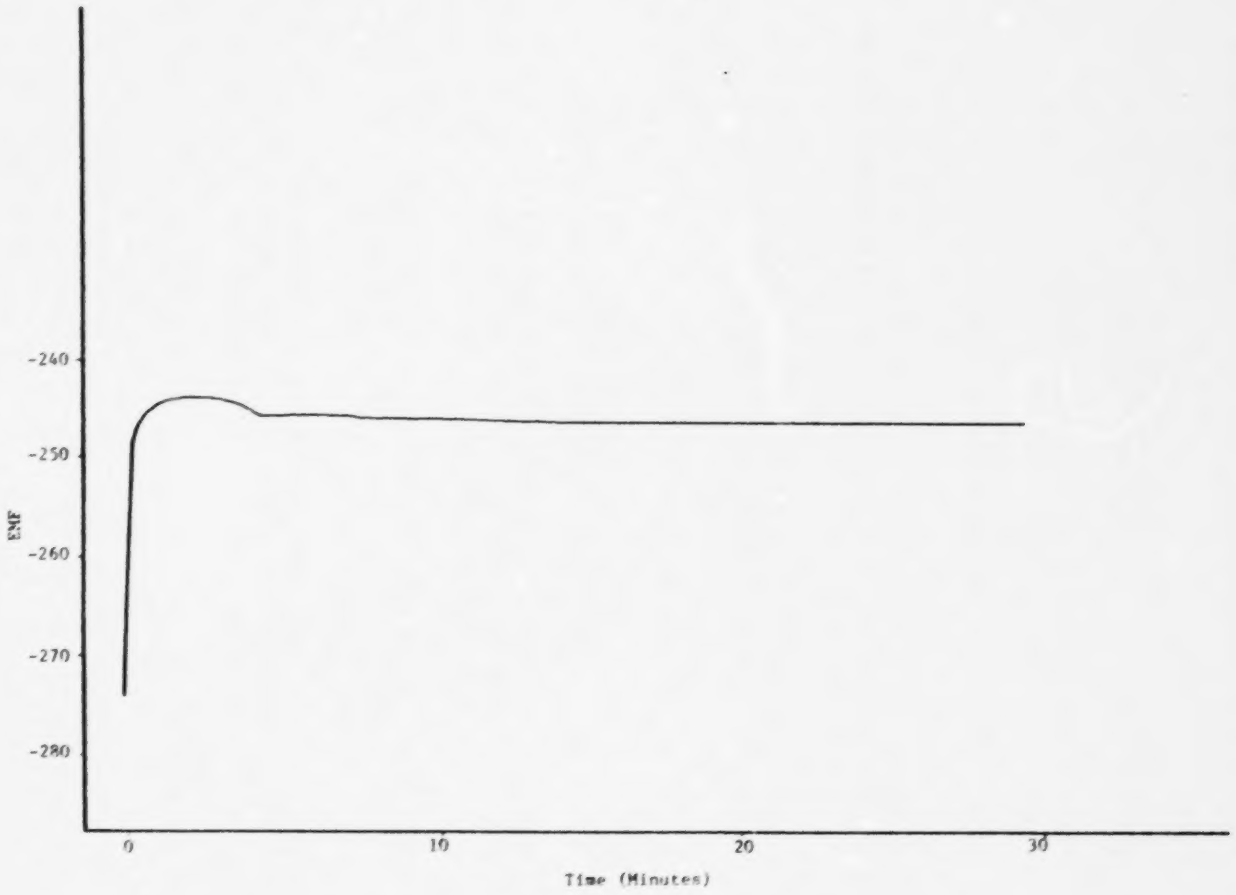
Run No. 1 - Deionized water

Run No. 2 - A 1:1 mixture of the final liquor of the first run and deionized water

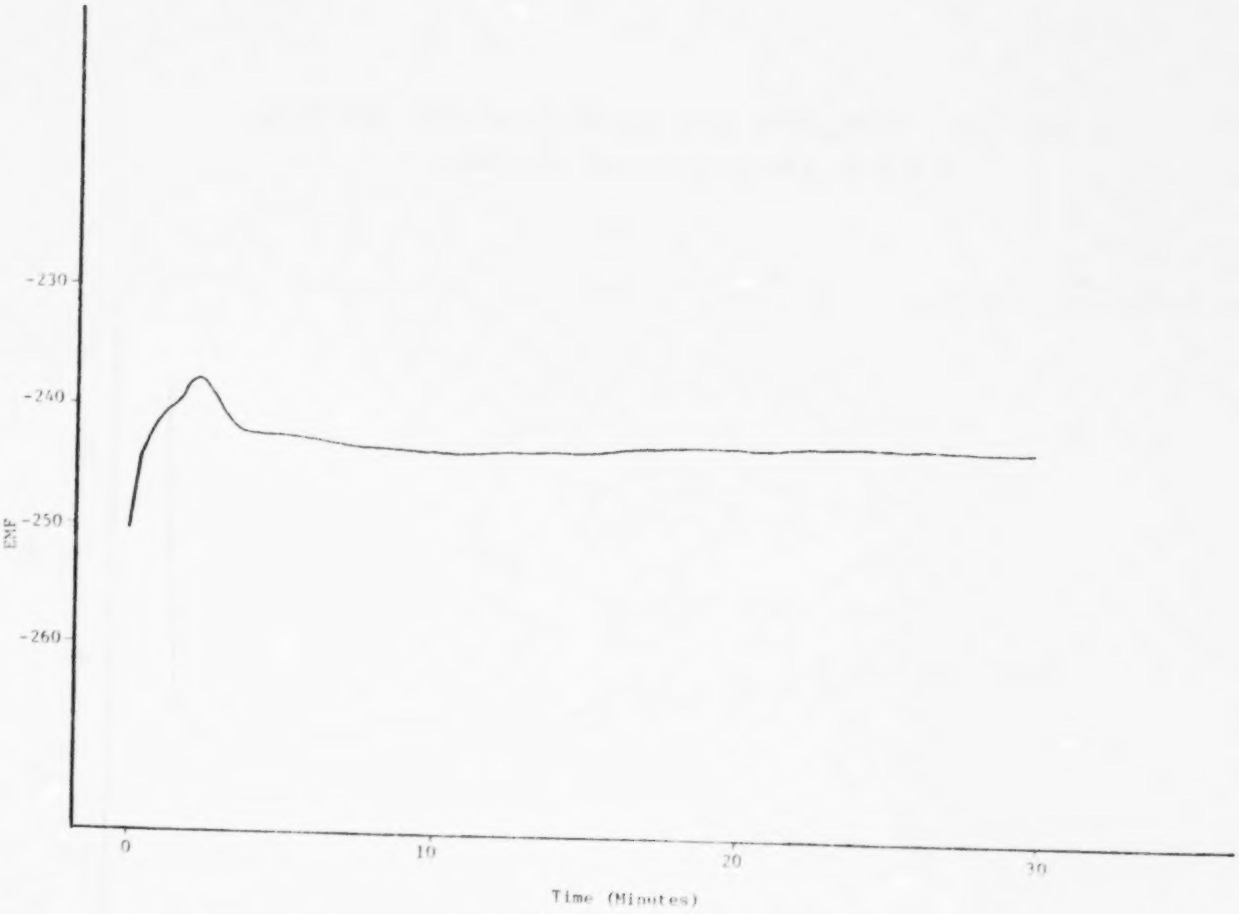
Run No. 3 - 25 ppm carbonate (0.417 mmole/ℓ)
500 ppm sulfate (5.21 mmole/ℓ)
259 ppm sodium (11.3 mmole/ℓ)

Run No. 4 - 25 ppm carbonate (0.417 mmole/ℓ)
2500 ppm sulfate (26.0 mmole/ℓ)
1220 ppm sodium (52.8 mmole/ℓ)

Run No. 5 - 100 ppm carbonate (1.67 mmole/ℓ)
500 ppm sulfate (5.21 mmole/ℓ)
316 ppm sodium (13.8 mmole/ℓ)



COMANCHE STEAM-ELECTRIC STATION
DIVALENT CATION SPECIFIC ION ELECTRODE - RUN NO. 1



COMANCHE STEAM-ELECTRIC STATION
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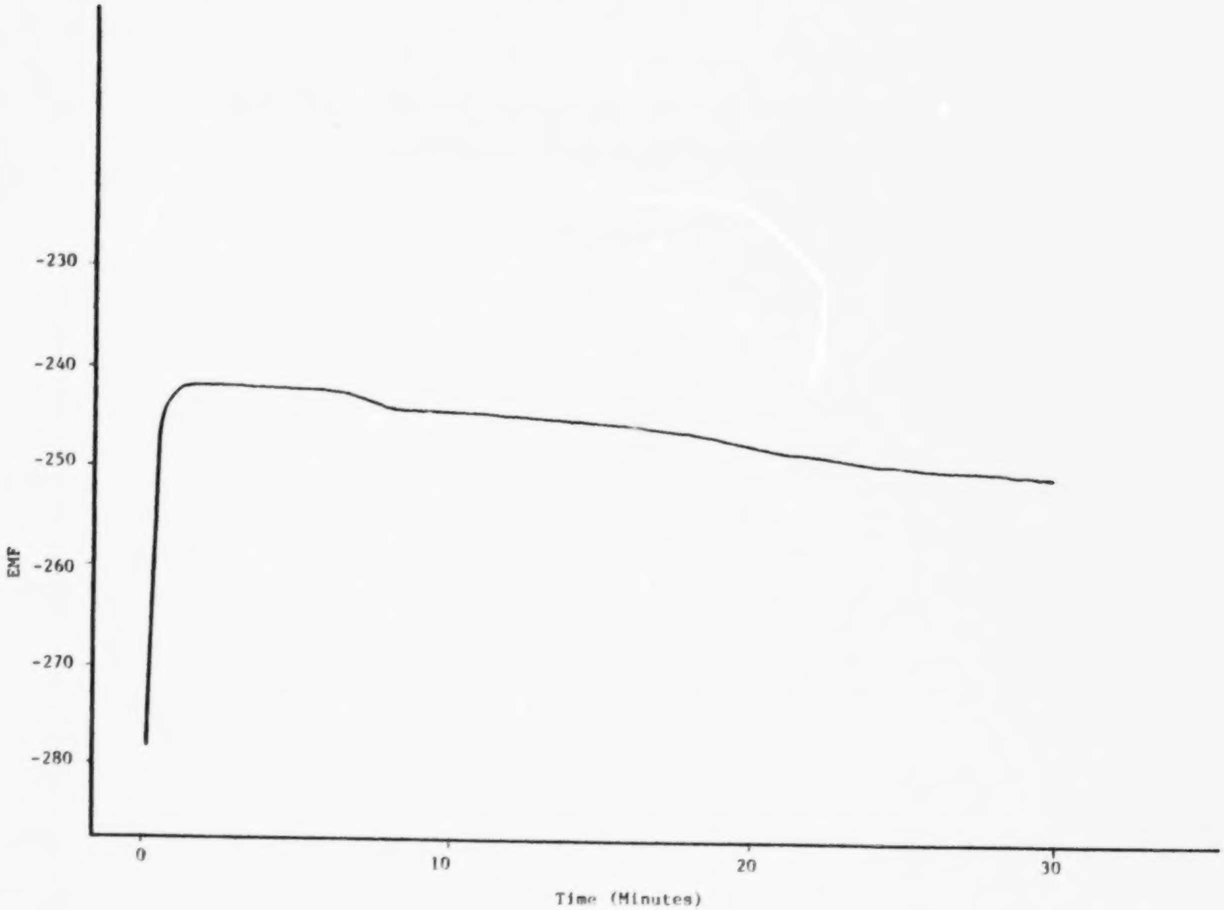
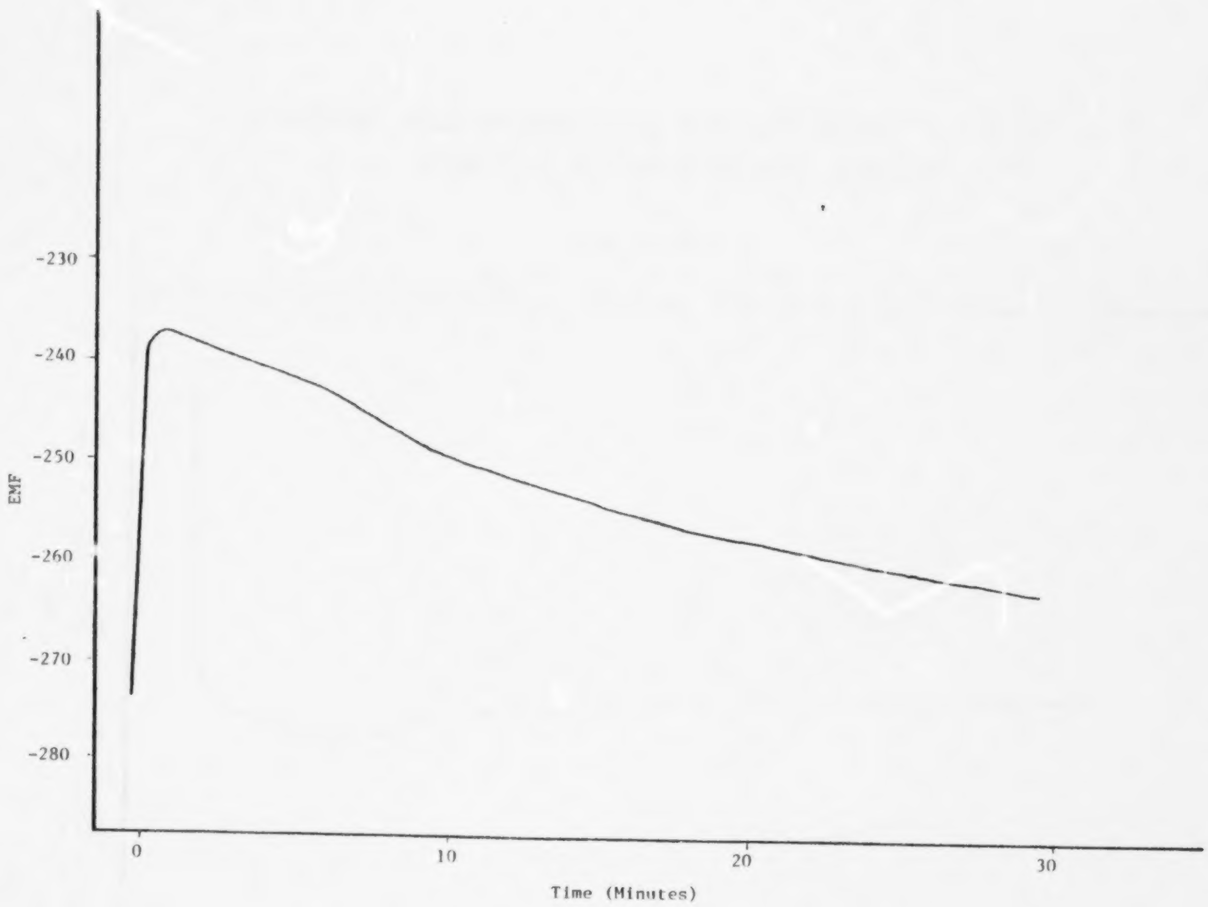
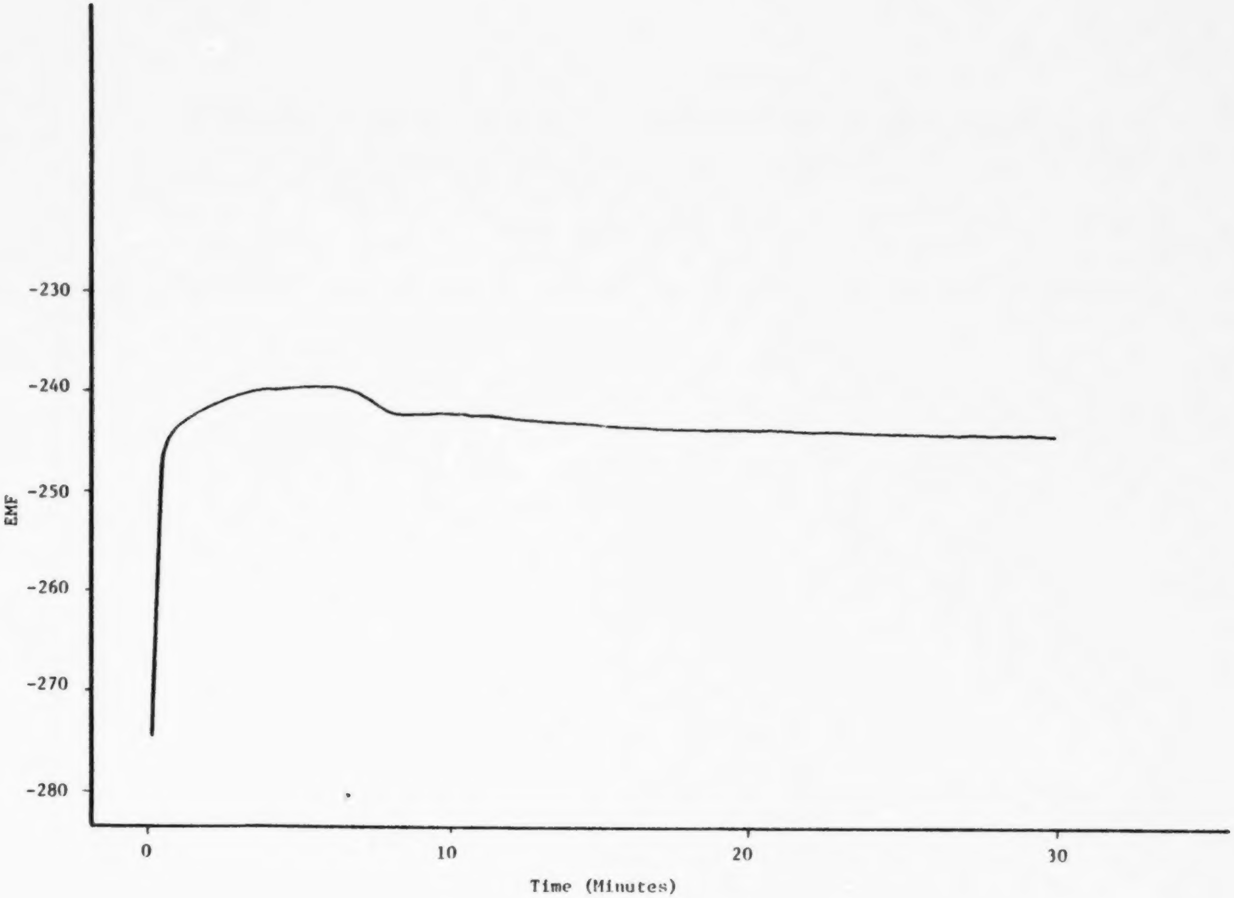


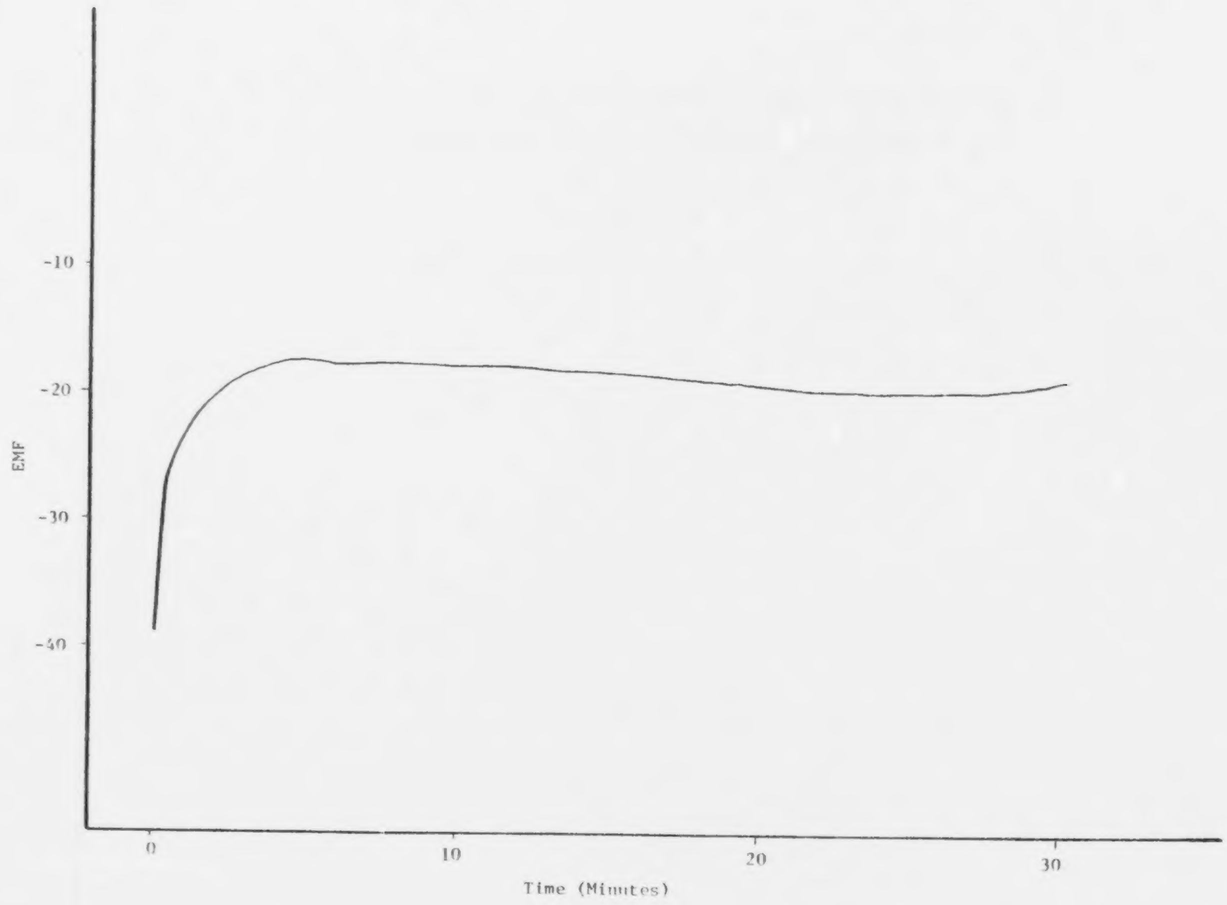
COMANCHE STEAM-ELECTRIC STATION
DIVALENT CATION SPECIFIC ION ELECTRODE - RUN NO. 3



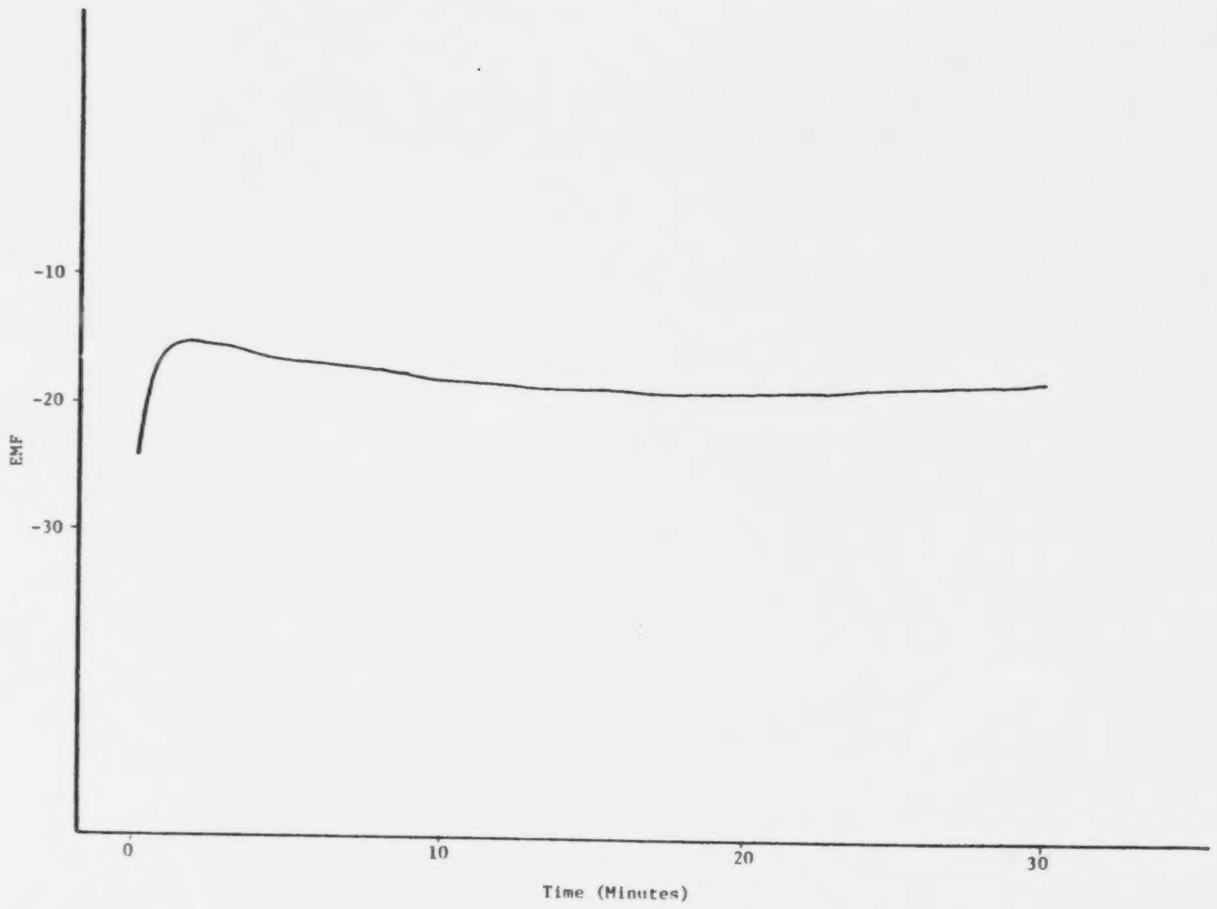
COMANCHE STEAM-ELECTRIC STATION
DIVALENT CATION SPECIFIC ION ELECTRODE - RUN NO. 4



COMANCHE STEAM-ELECTRIC STATION
DIVALENT CATION SPECIFIC ION ELECTRODE - RUN NO. 5



COMANCHE STEAM-ELECTRIC STATION
CALCIUM SPECIFIC ION ELECTRODE - RUN NO. 1



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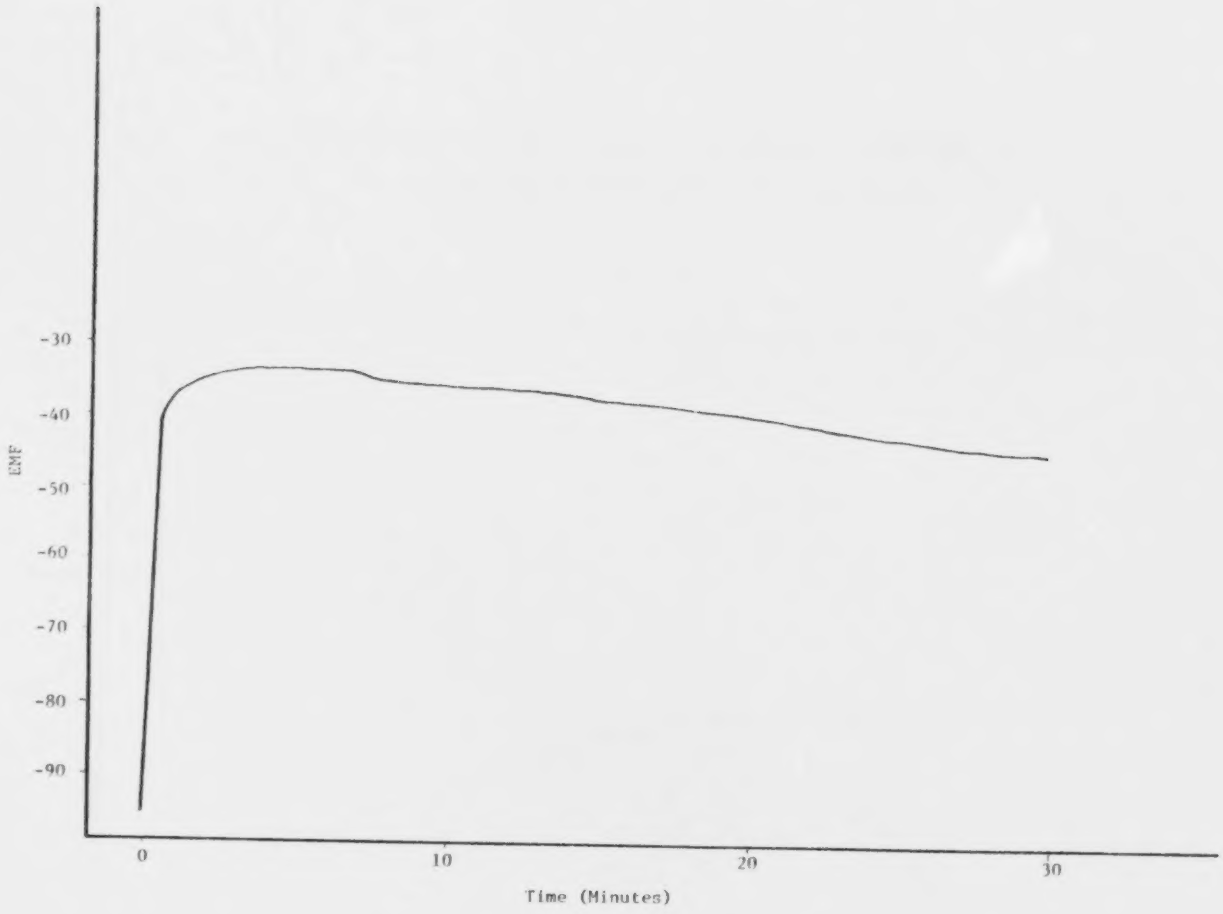

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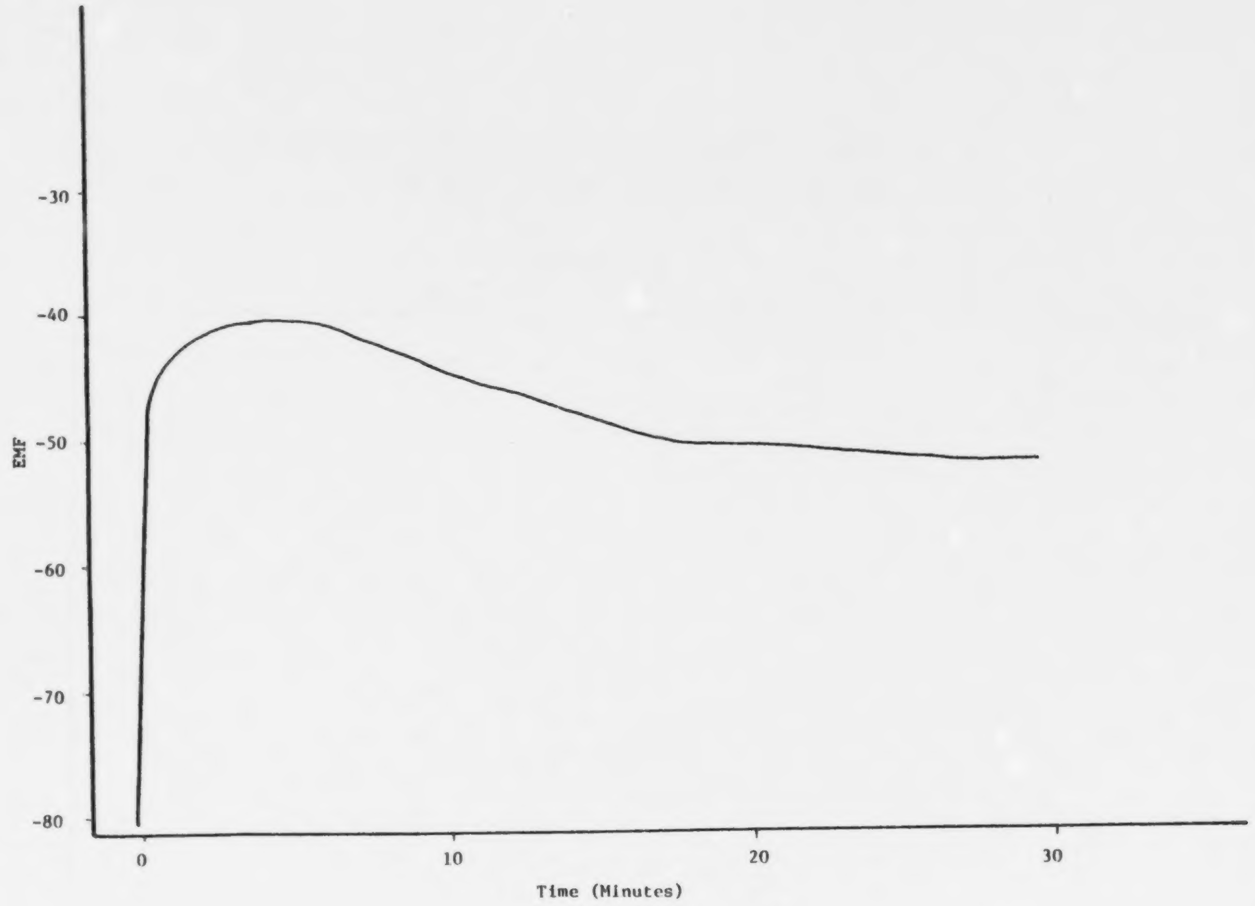

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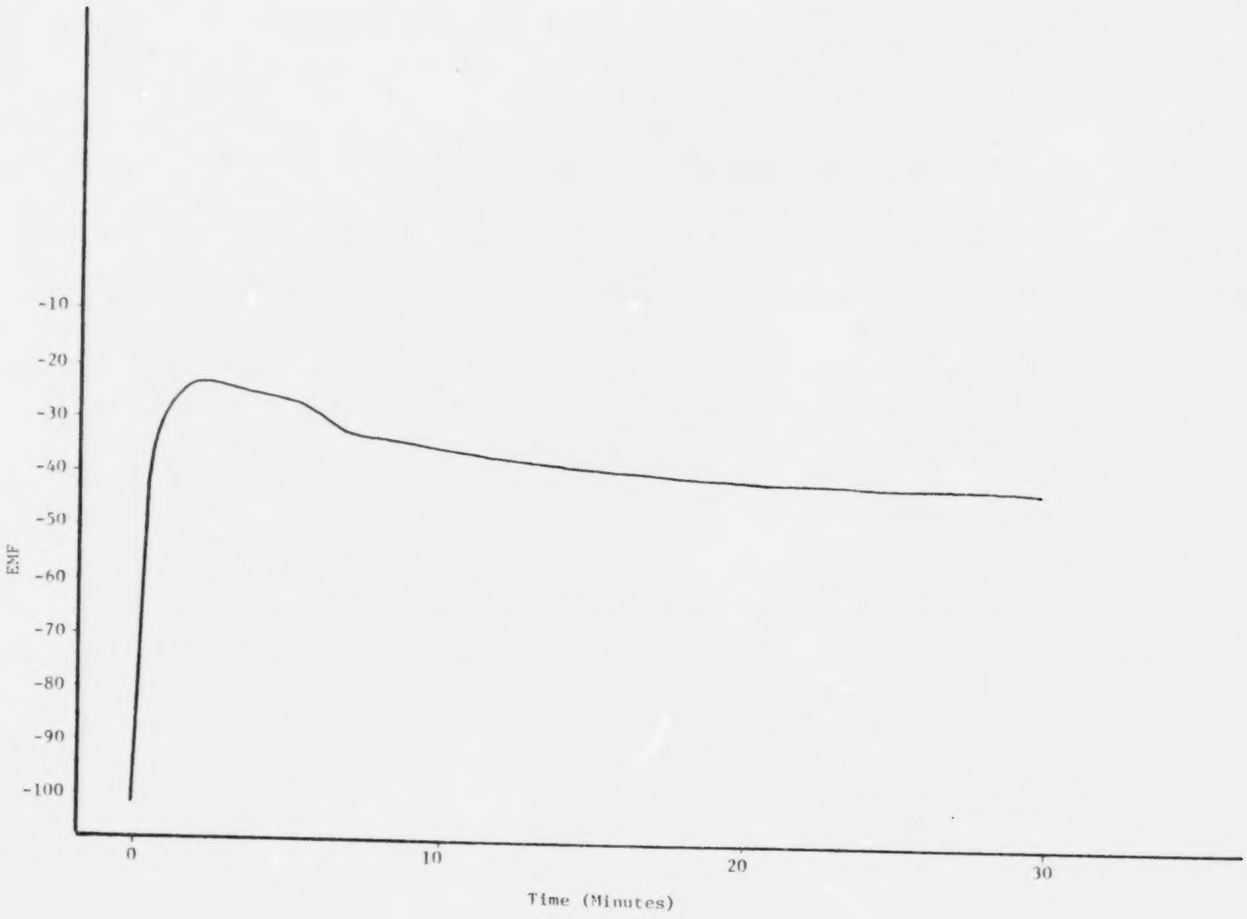

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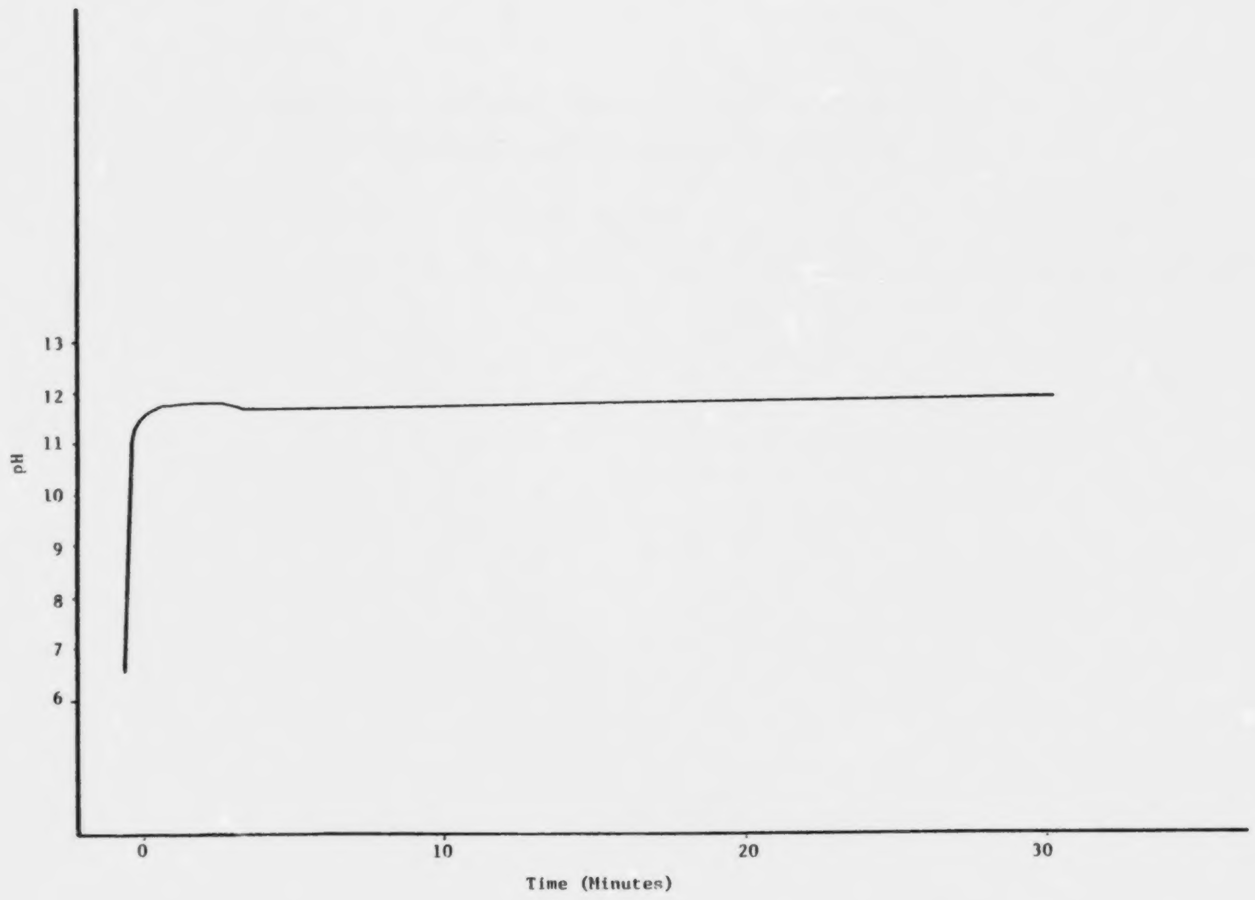
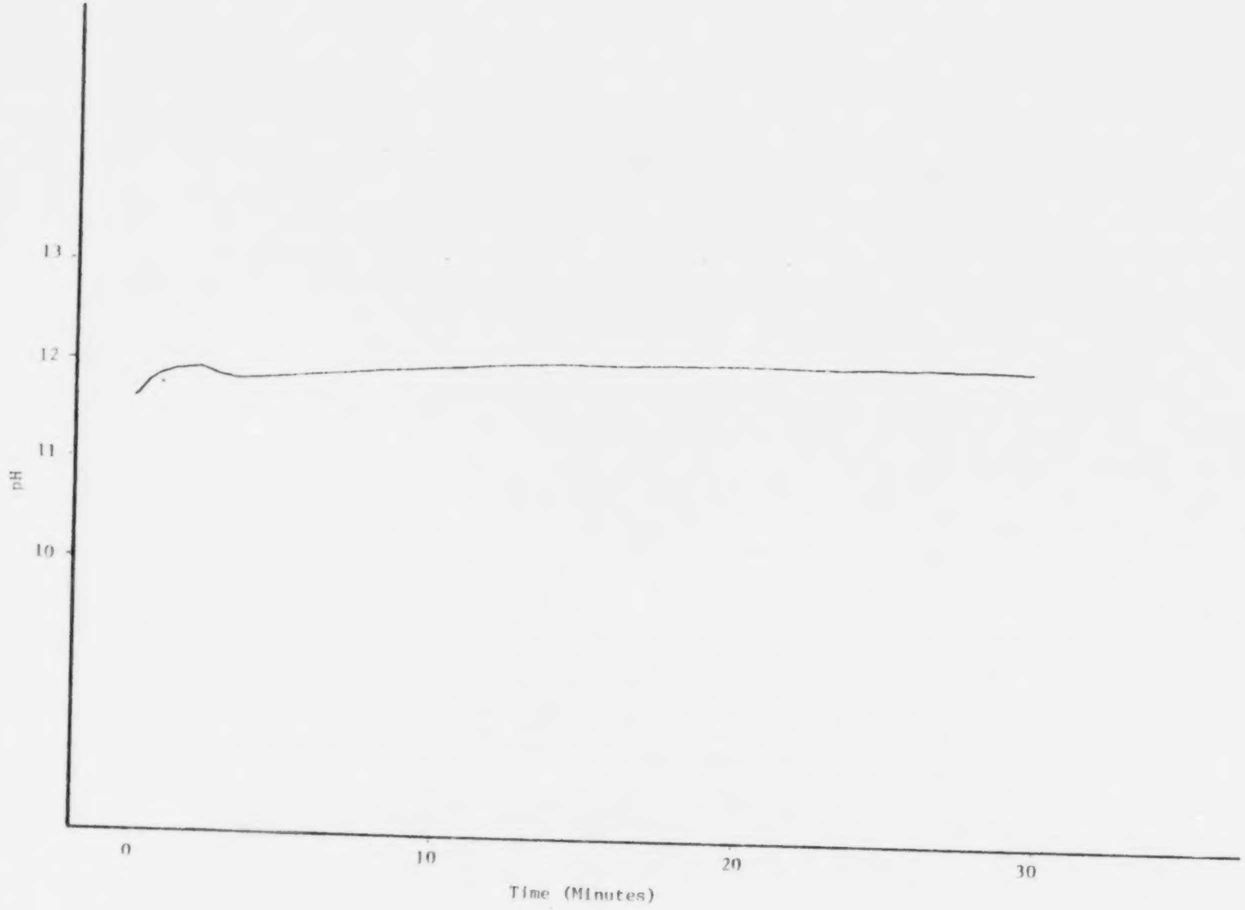


COMANCHE STEAM-ELECTRIC STATION
pH - RUN NO. 1



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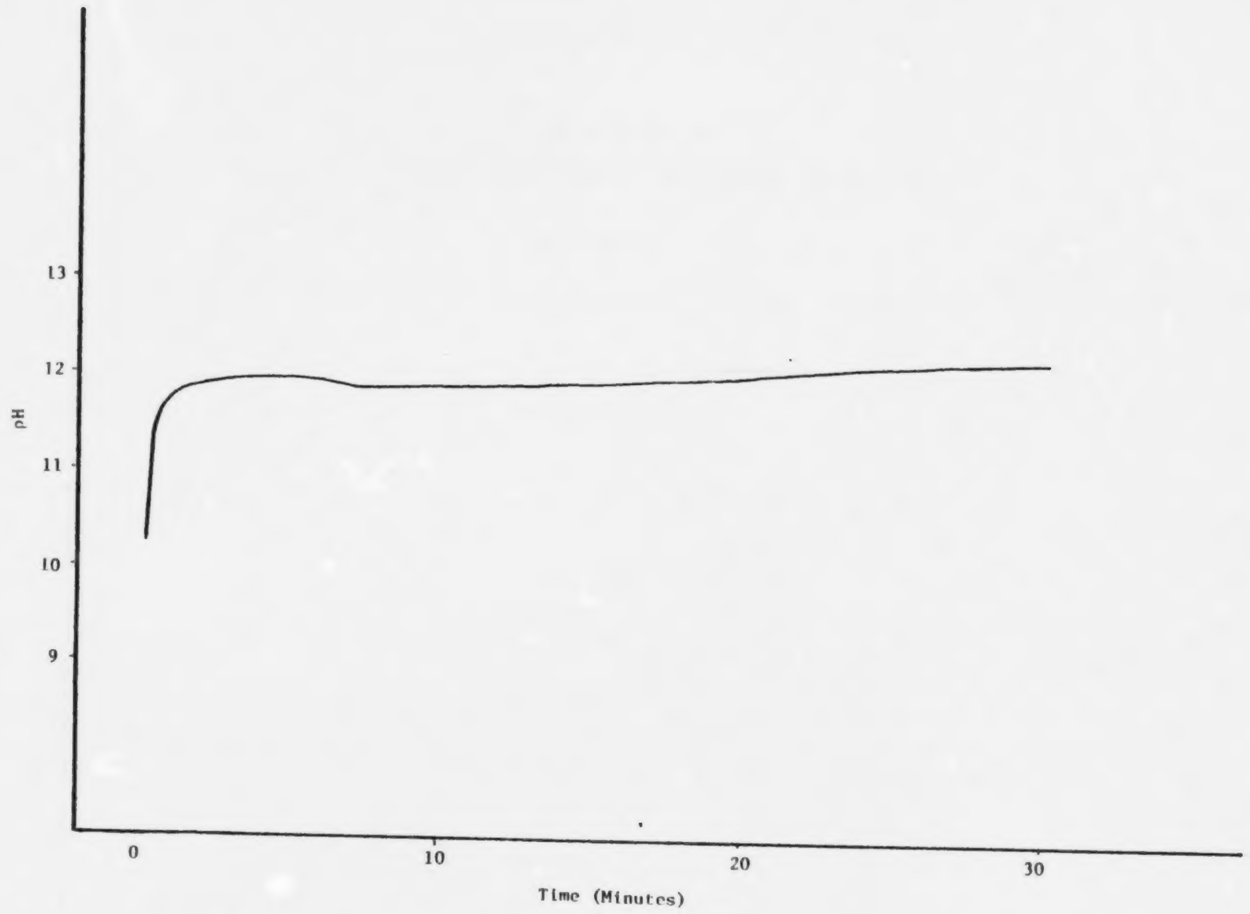
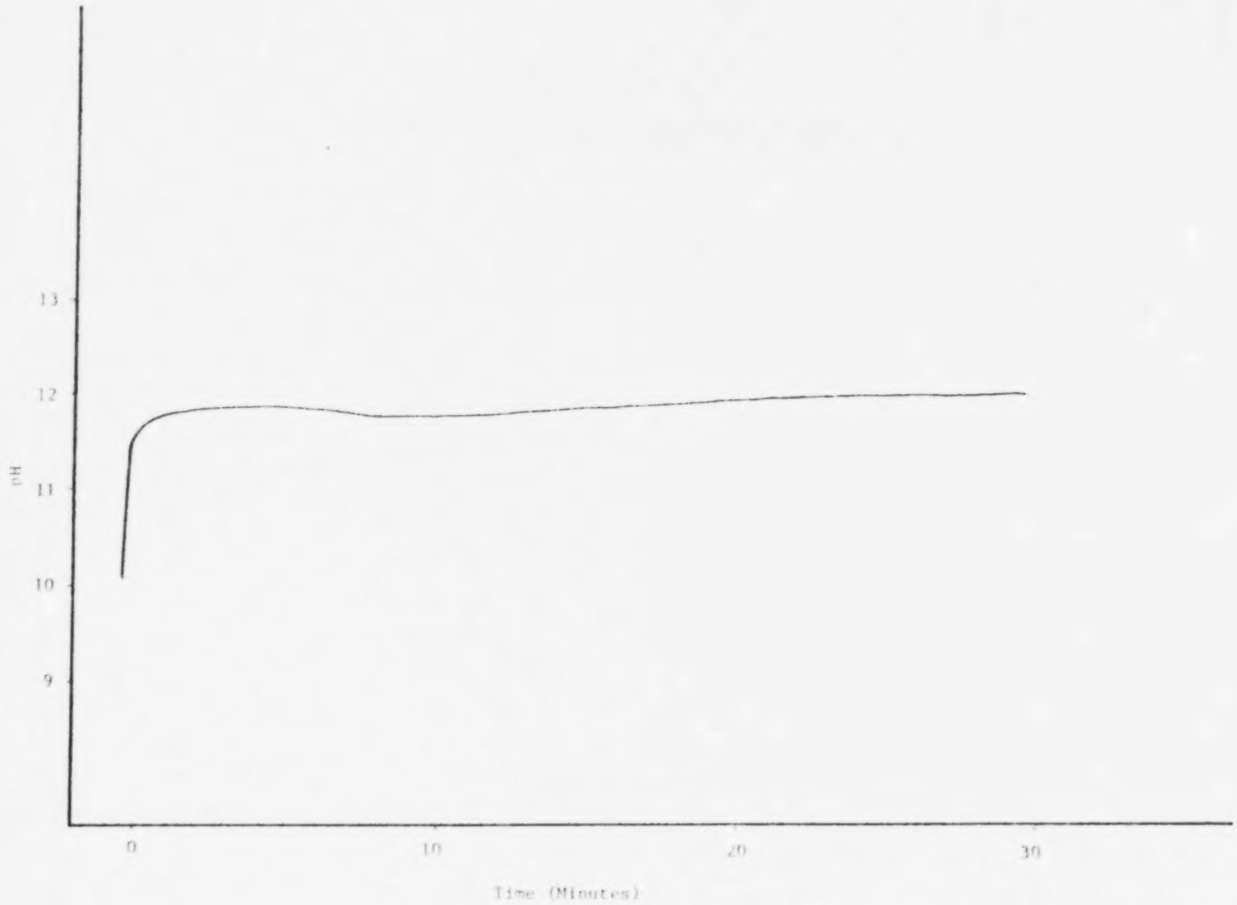


COMANCHE STEAM-ELECTRIC STATION
pH - RUN NO. 3



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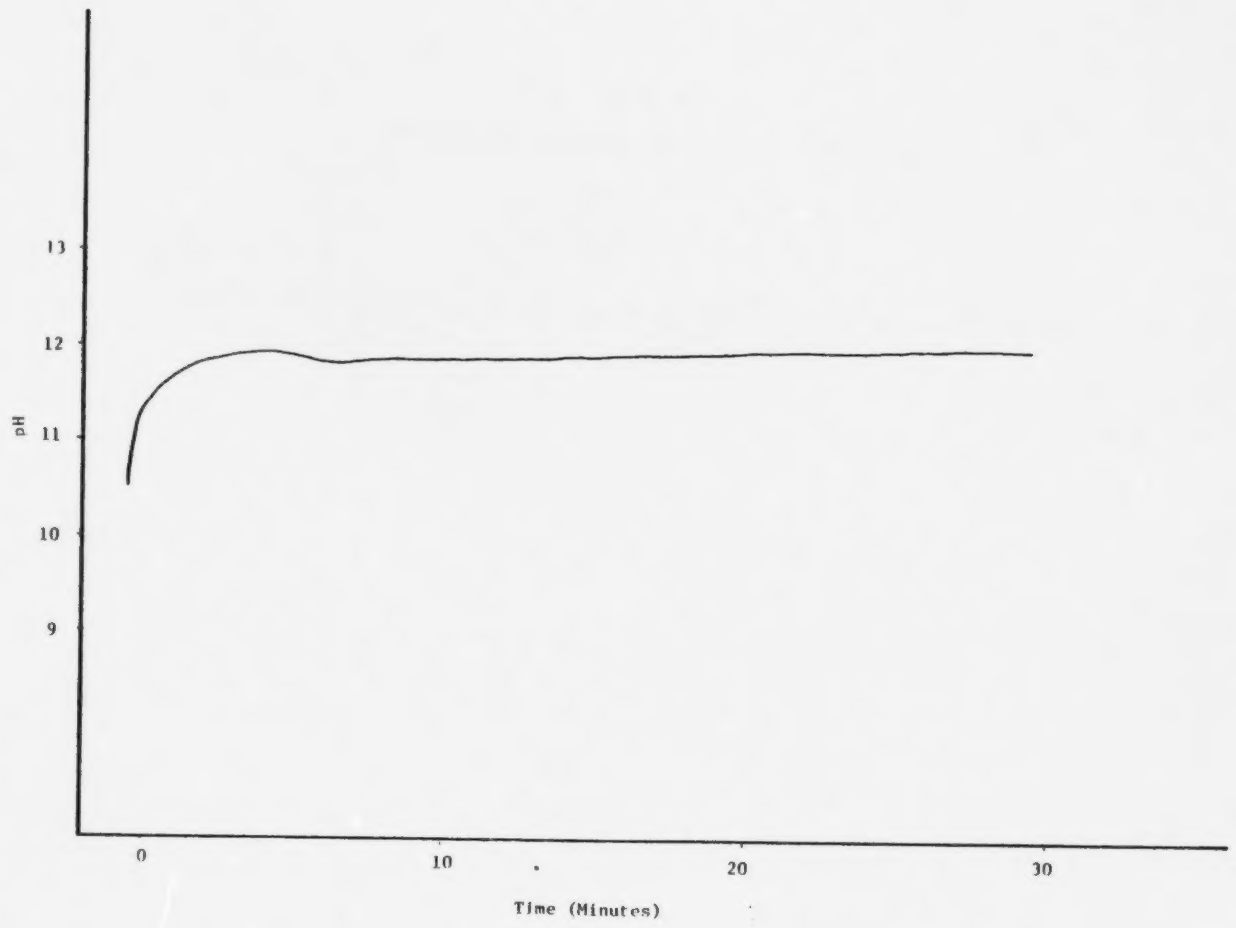
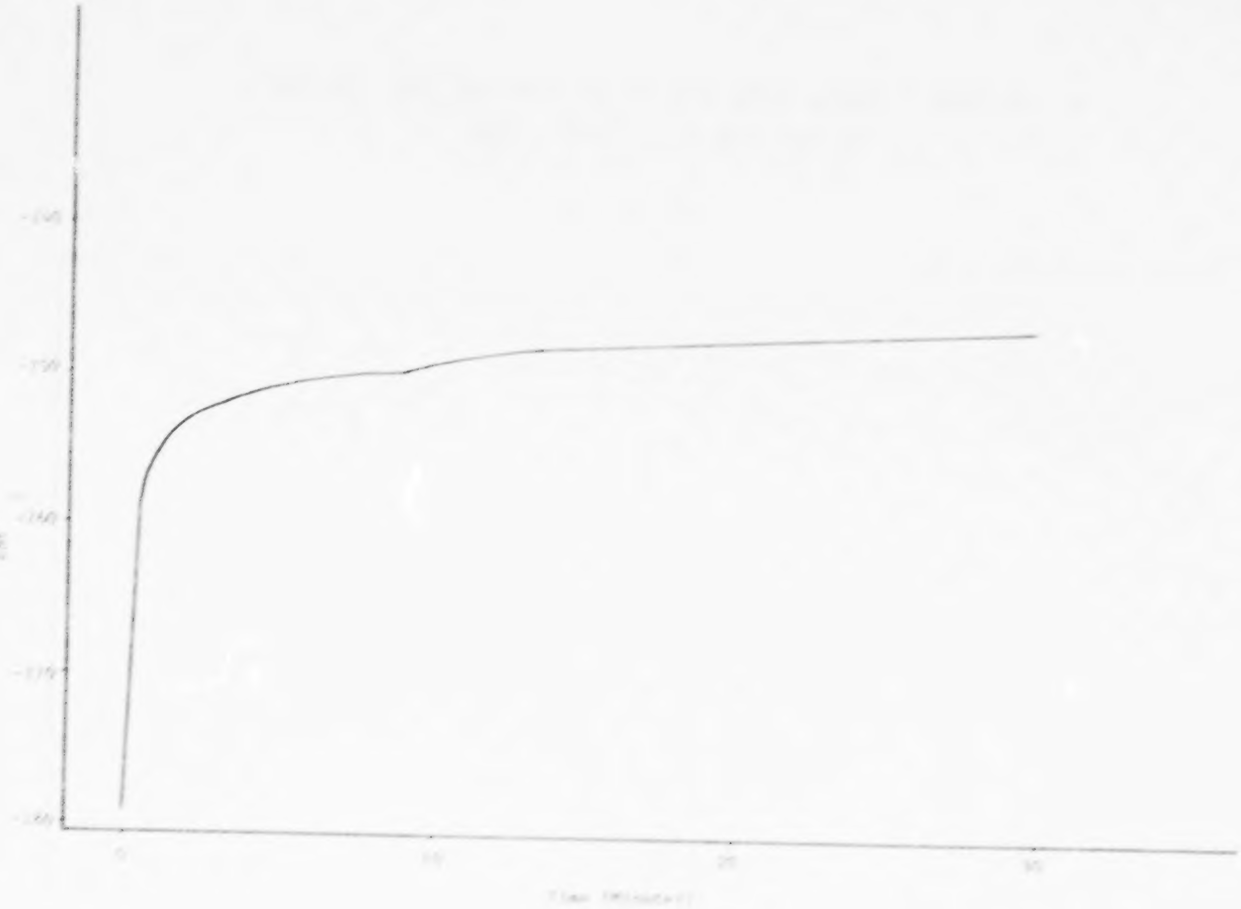
pH - RUN NO. 4

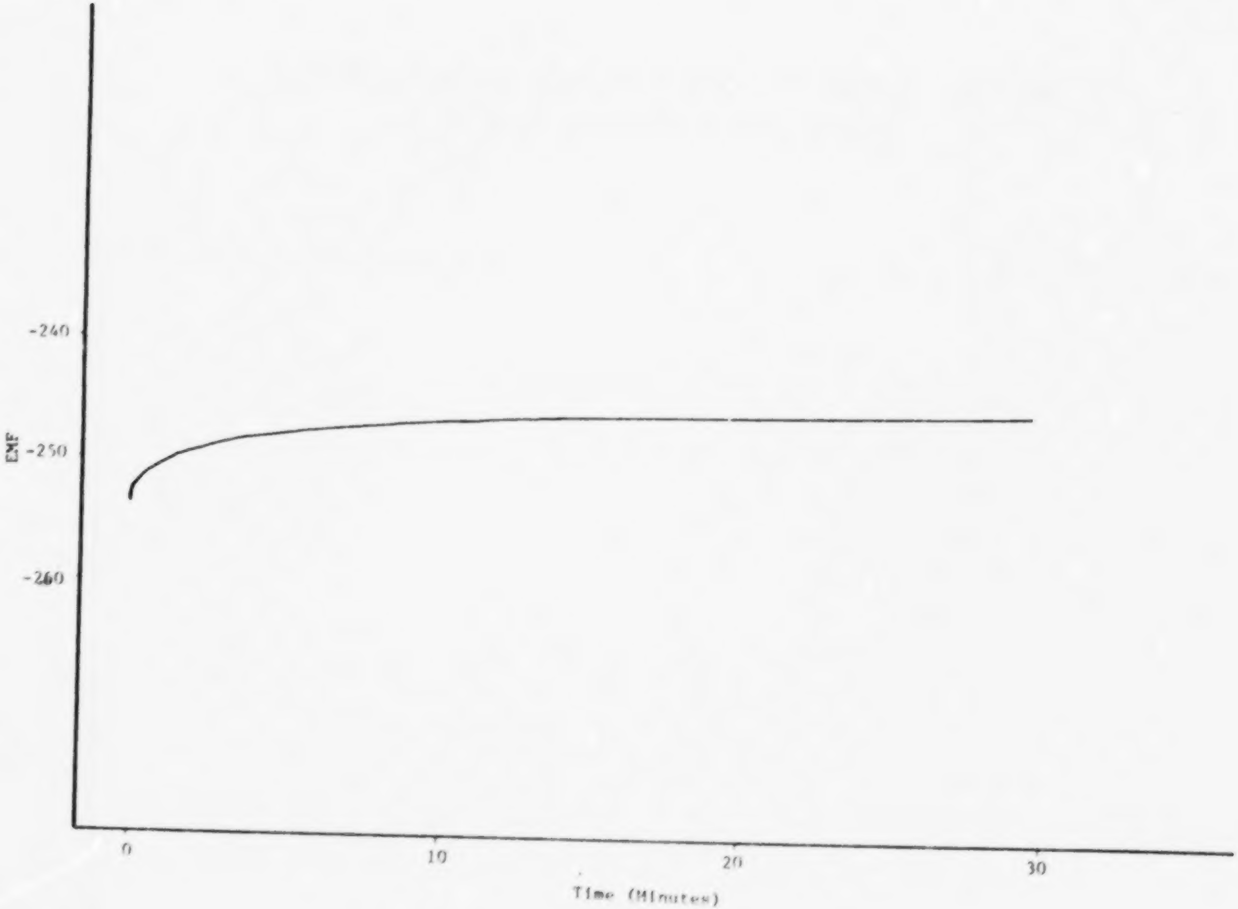


COMANCHE STEAM-ELECTRIC STATION
pH - RUN NO. 5



FOUR CORNERS POWER PLANT

DIVALENT CATION SPECIFIC ION ELECTRODE - RUN NO. 1



FOUR CORNERS POWER PLANT
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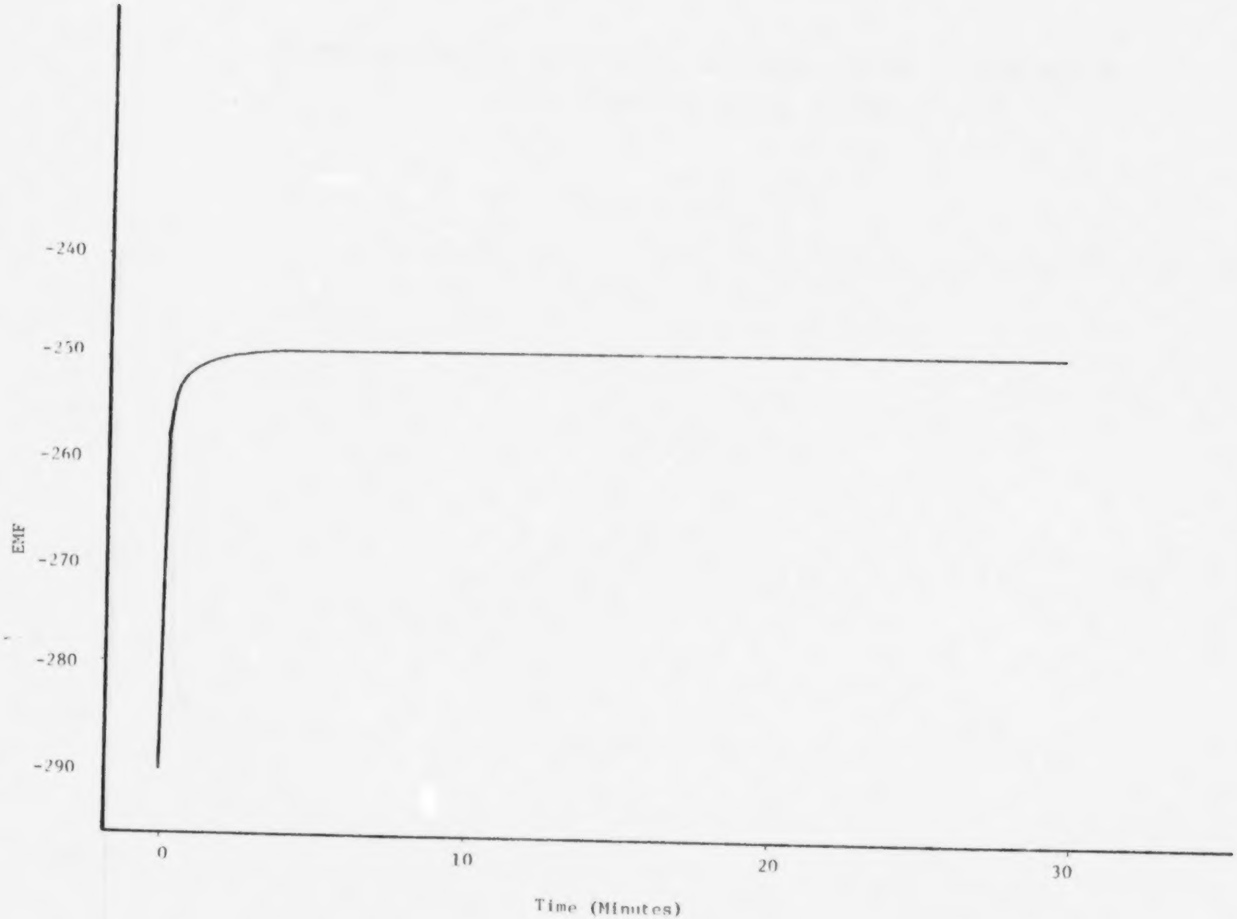

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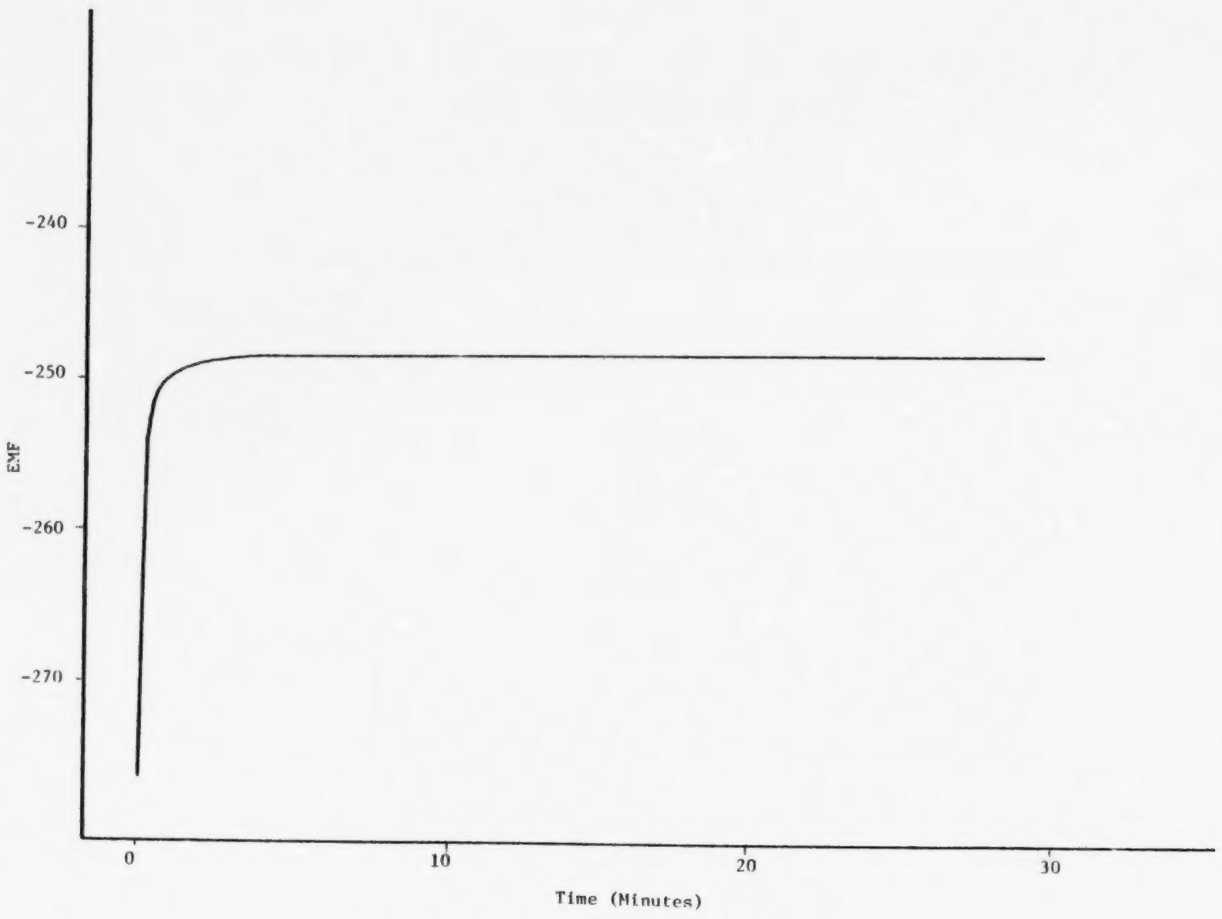

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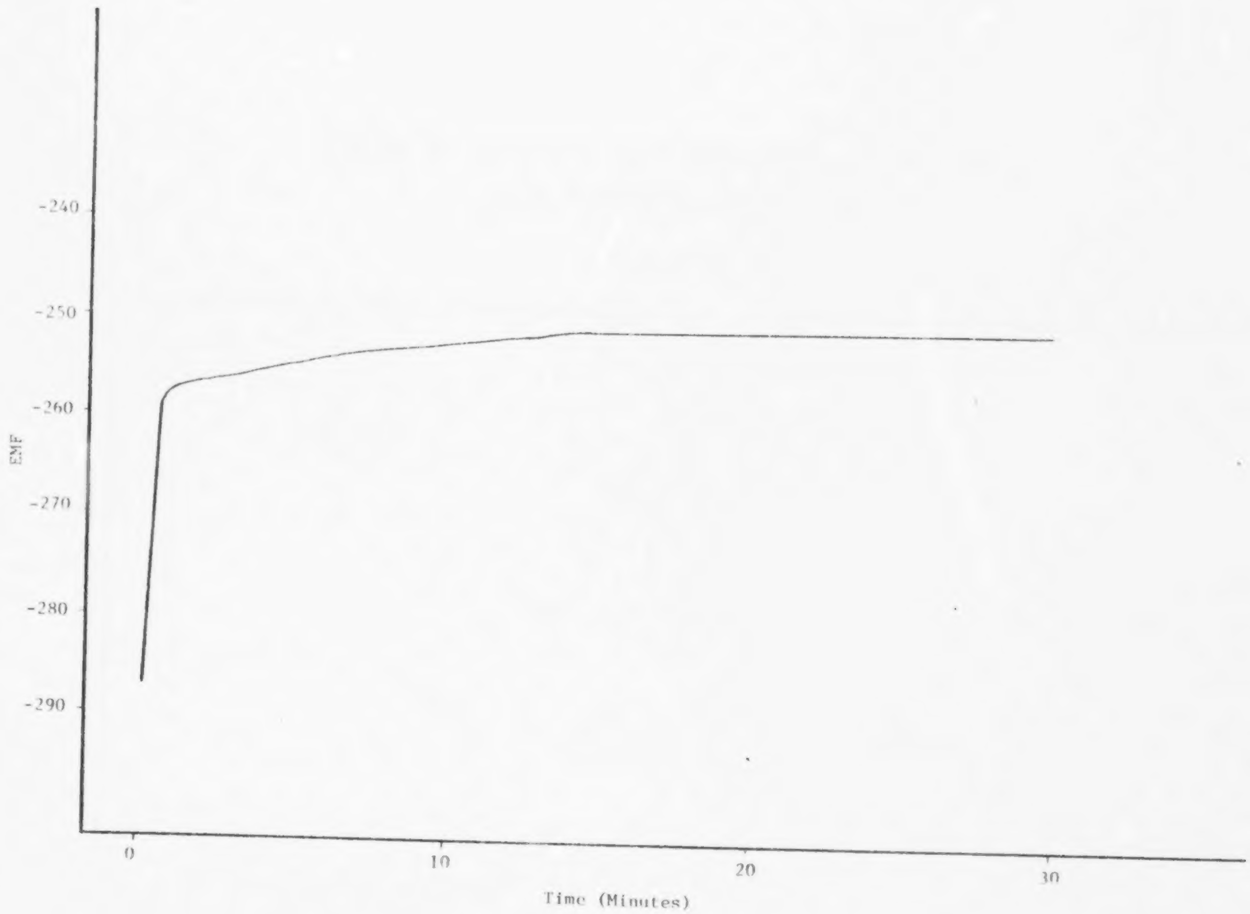
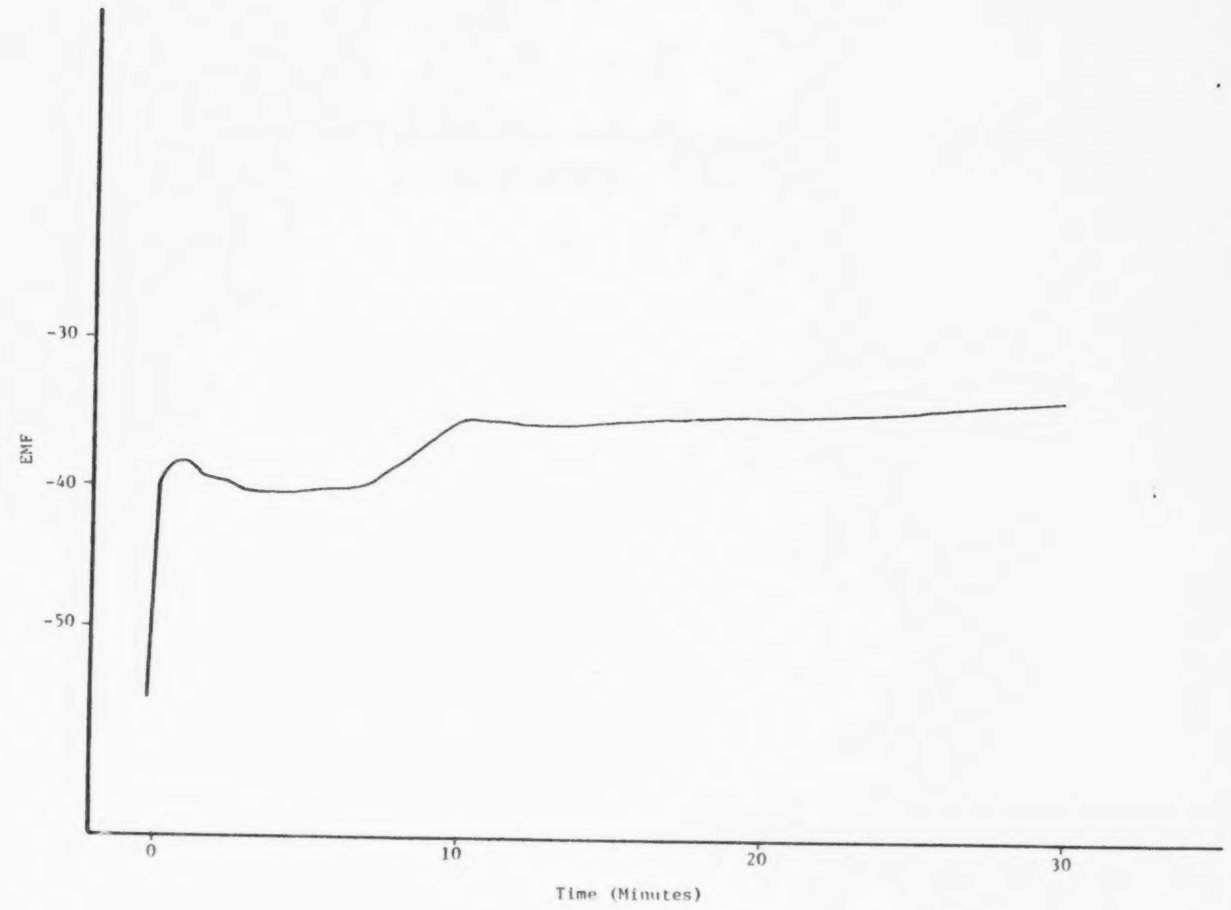


FOUR CORNERS POWER PLANT

DIVALENT CATION SPECIFIC ION ELECTRODE - RUN NO. 5



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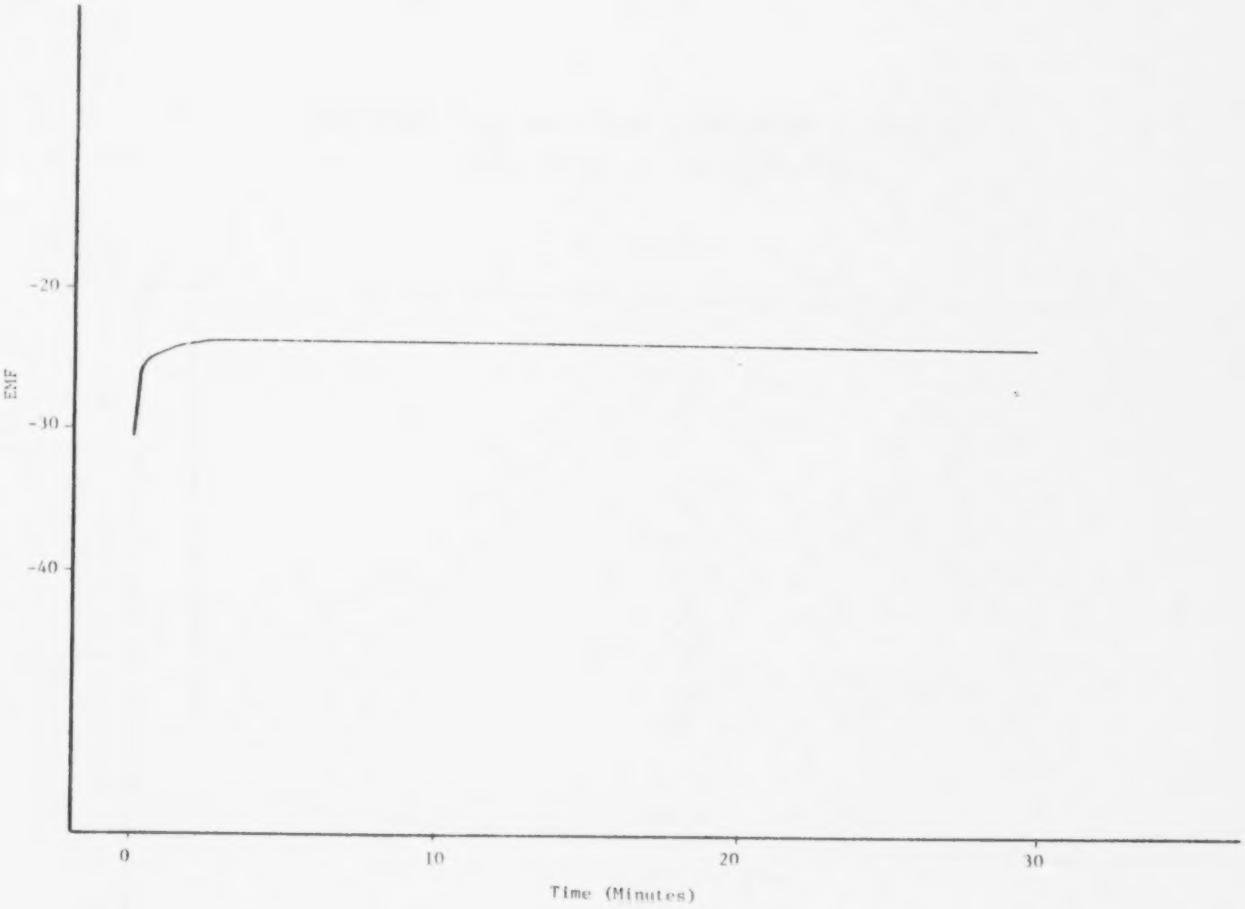
CALCIUM SPECIFIC ION ELECTRODE - RUN NO. 1



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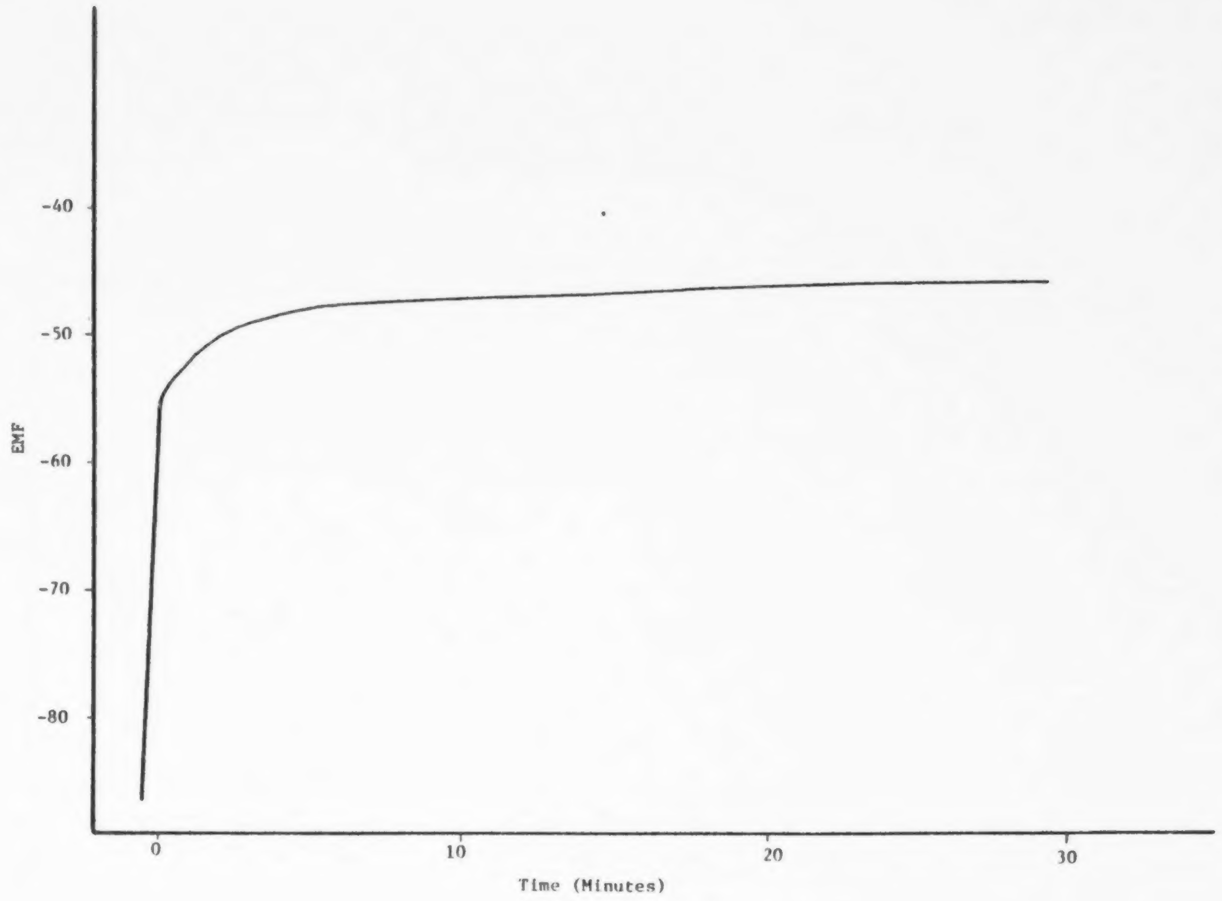

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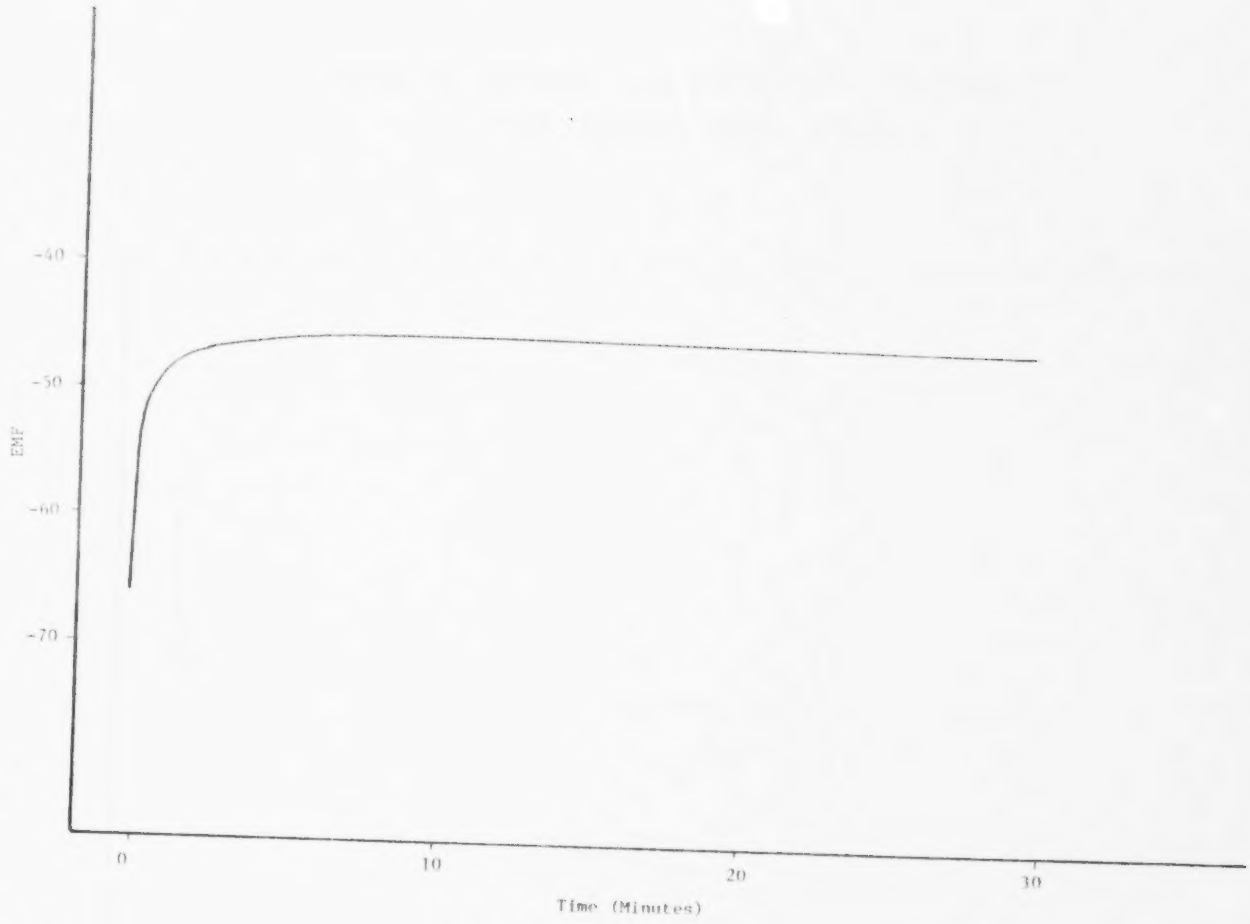

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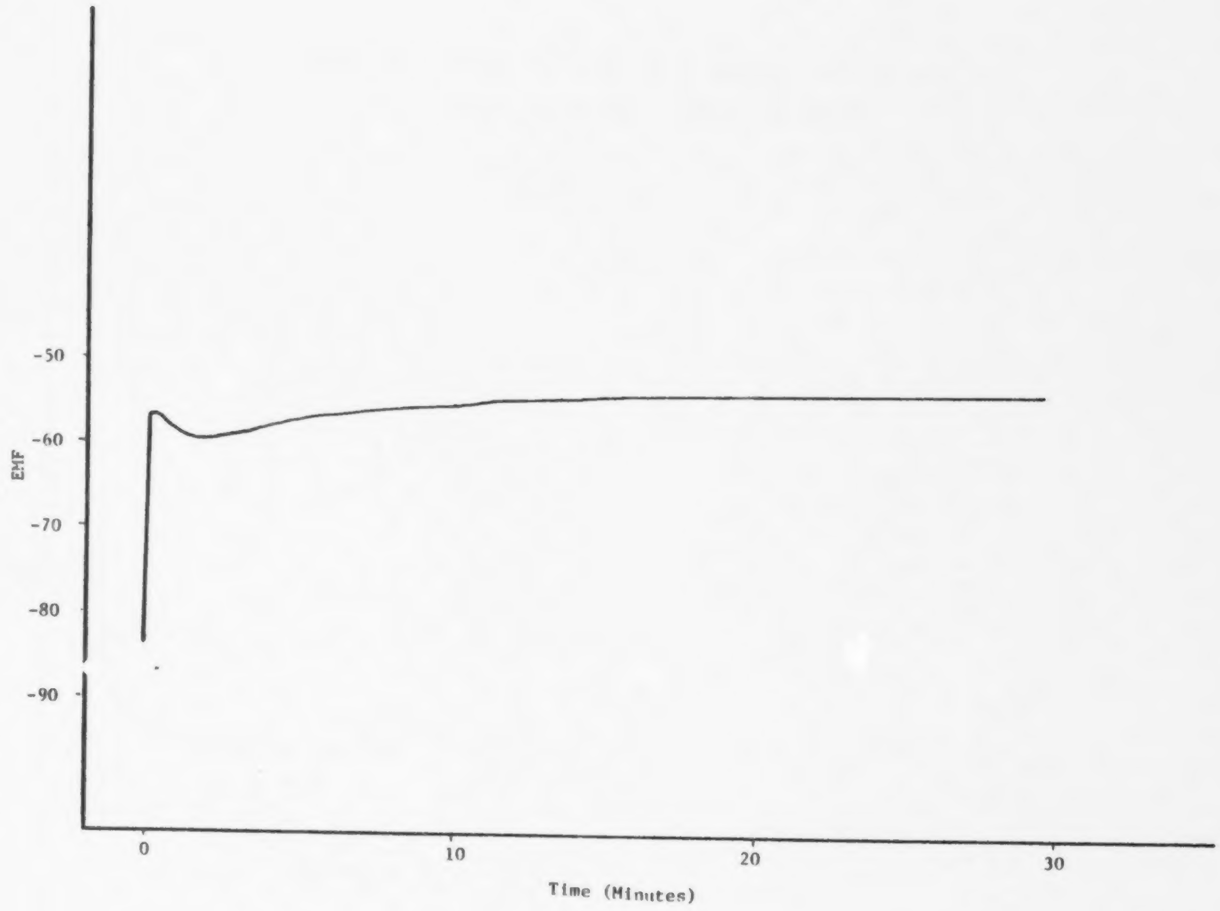

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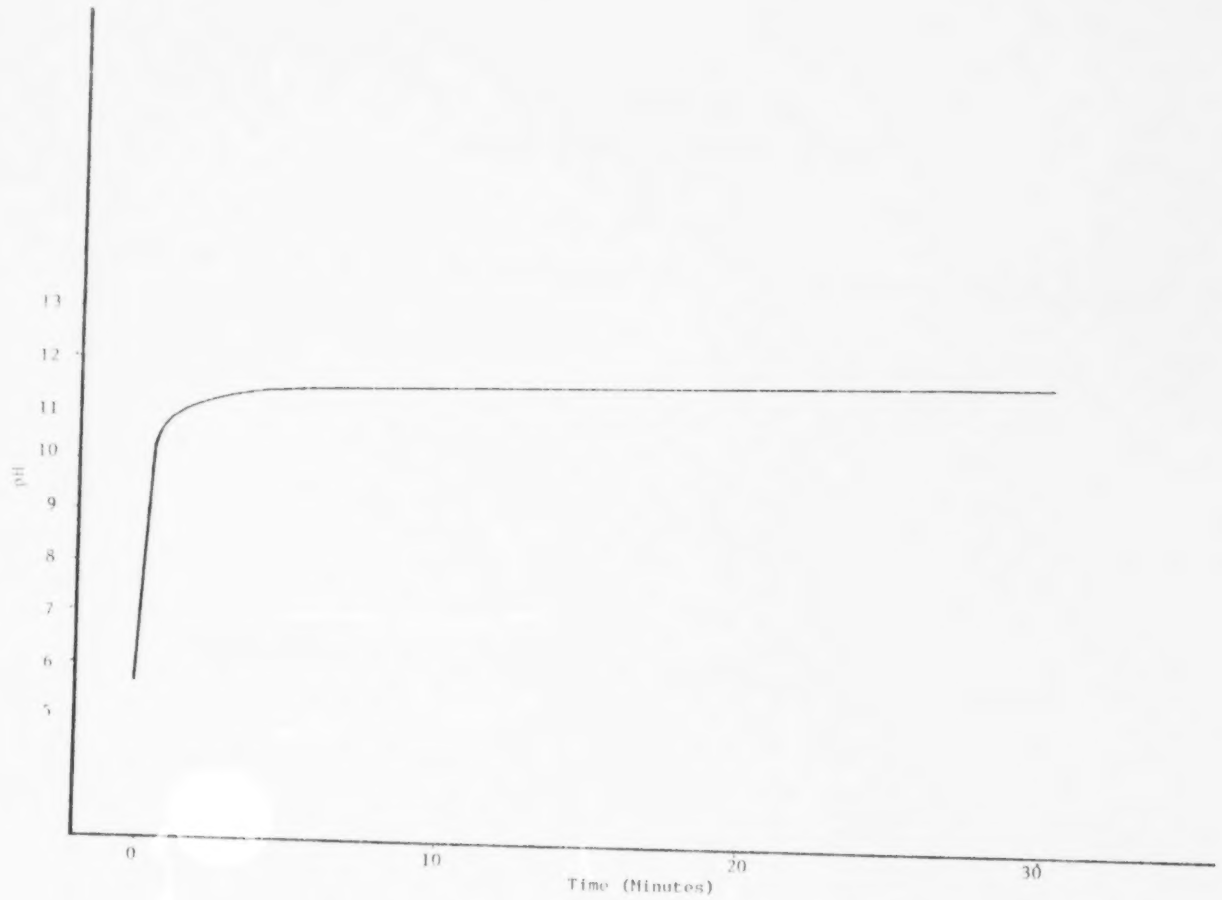
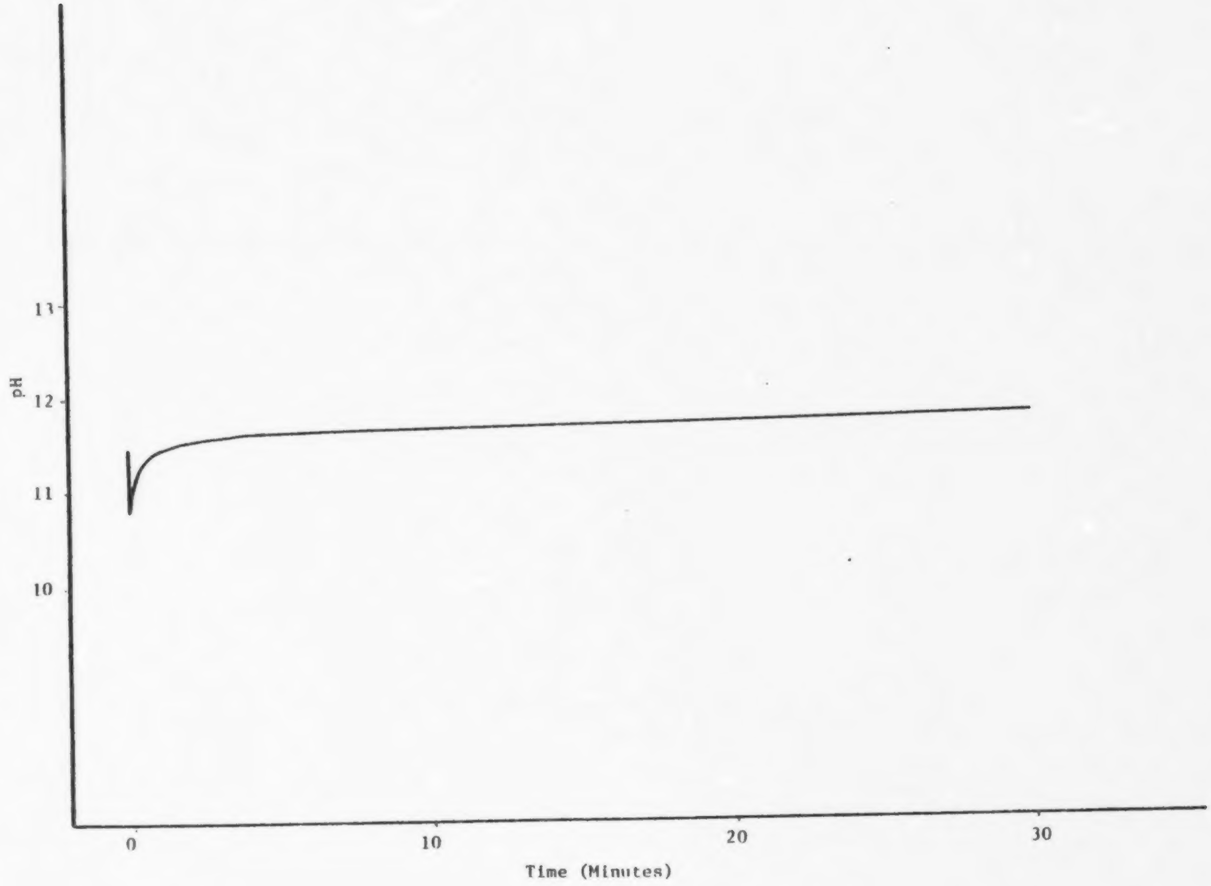
CALCIUM SPECIFIC ION ELECTRODE - RUN NO. 5



FOUR CORNERS POWER PLANT
pH - RUN NO. 1



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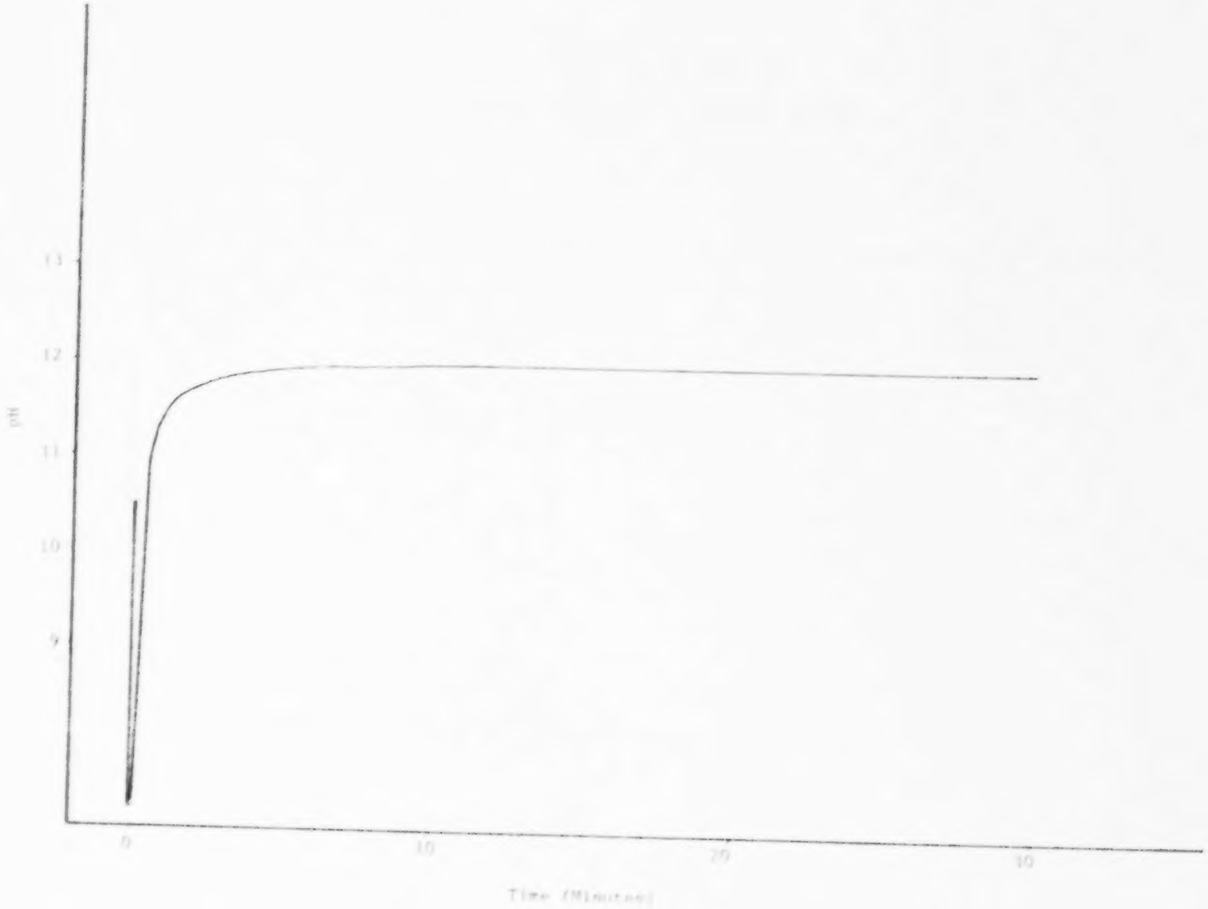

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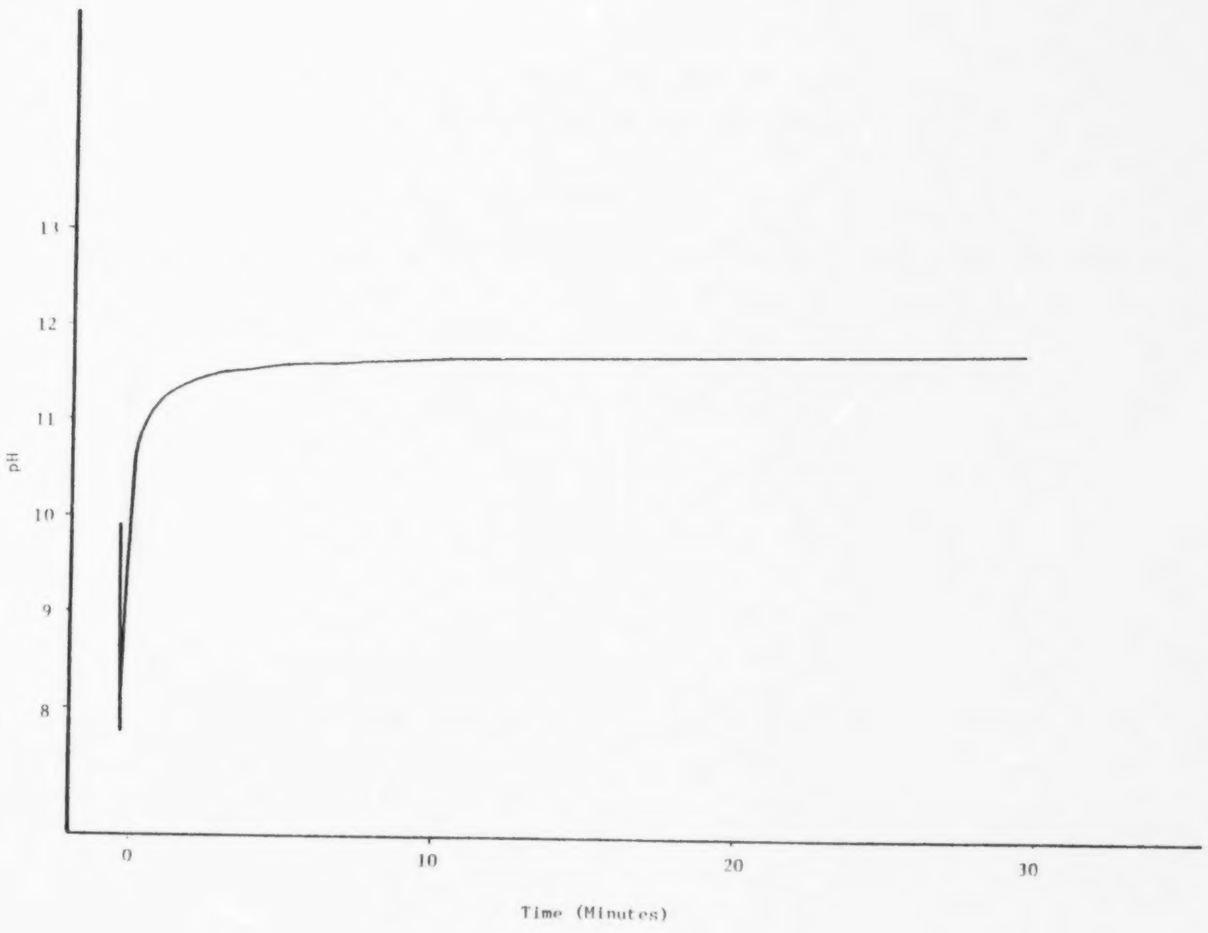
pH - RUN NO. 3



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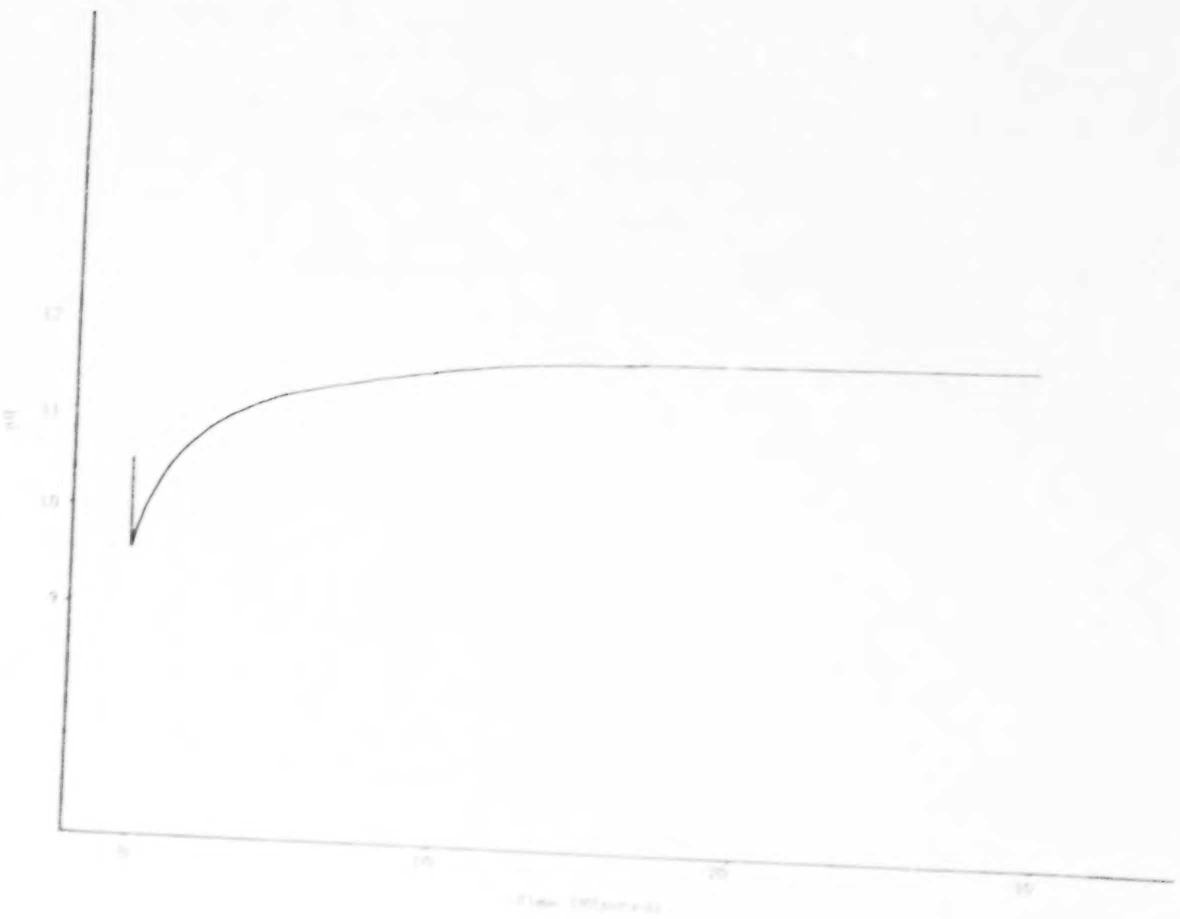

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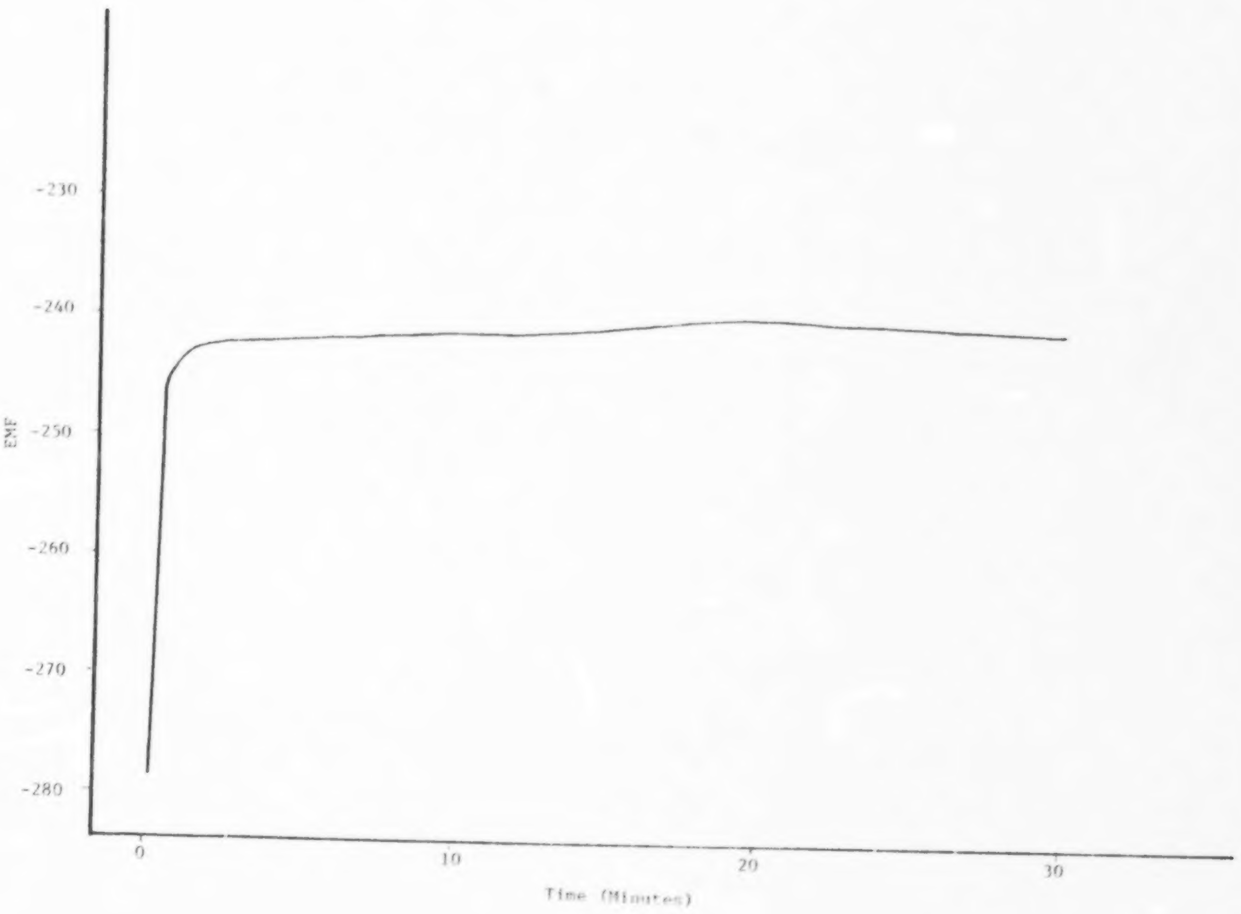
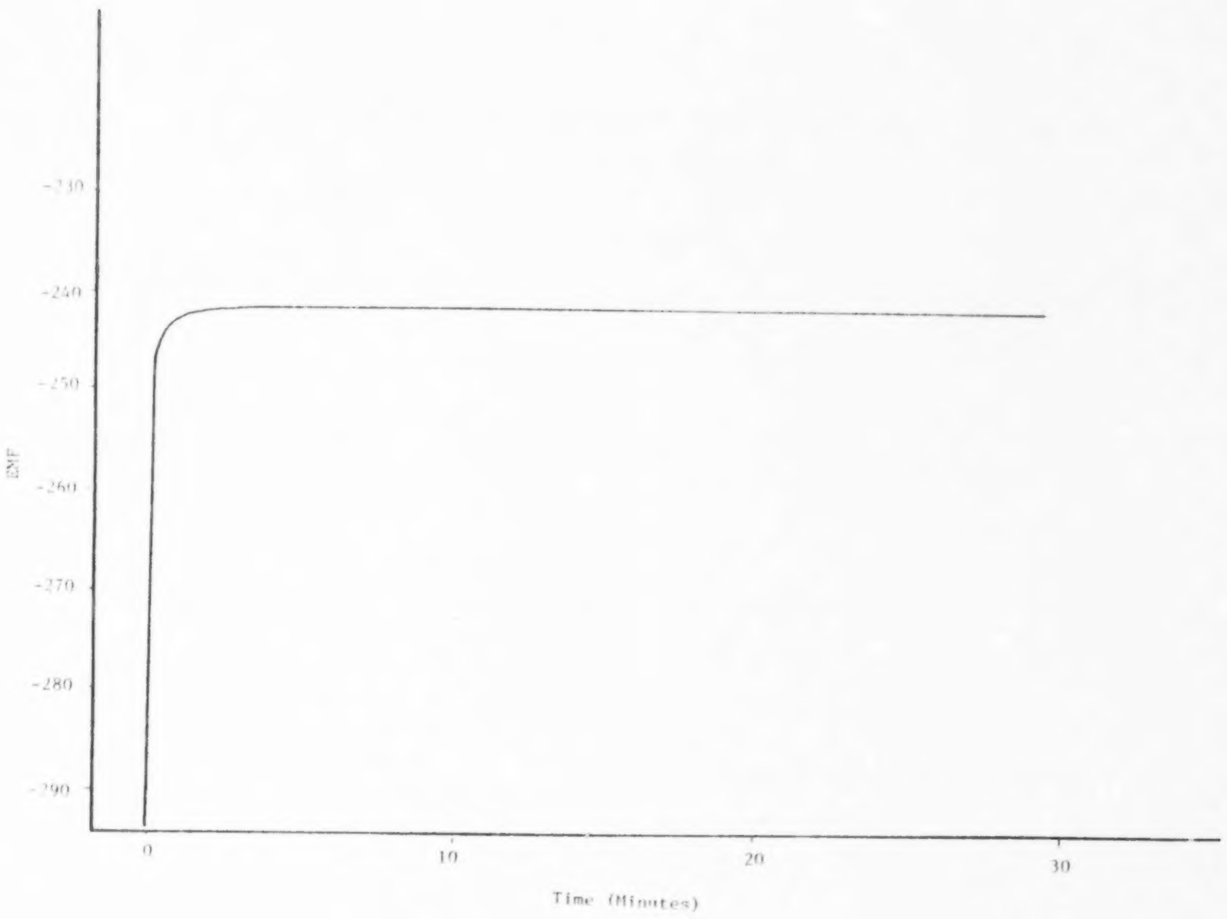
pH - RUN NO. 5



PLANT BOWEN
DIVALENT CATION SPECIFIC ION ELECTRODE - RUN NO. 1



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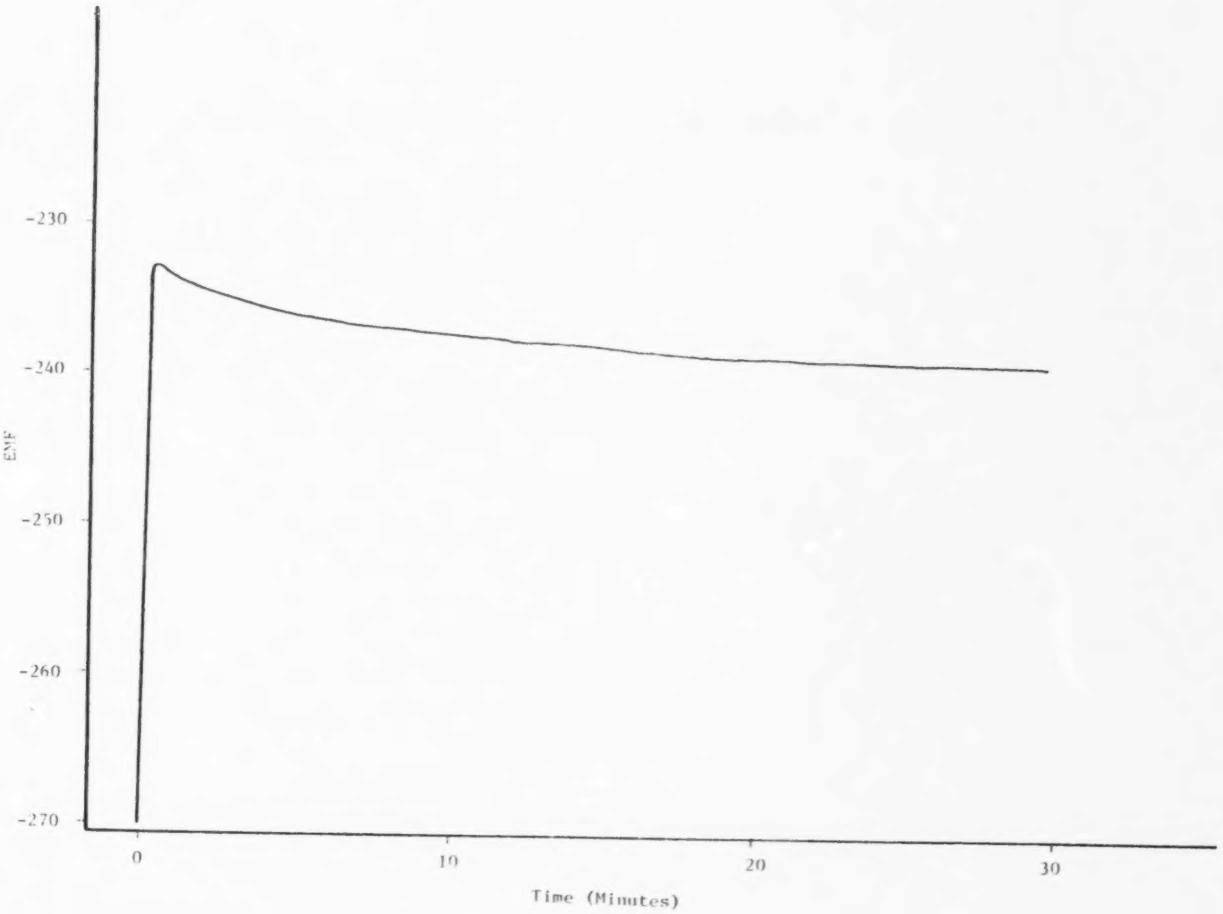

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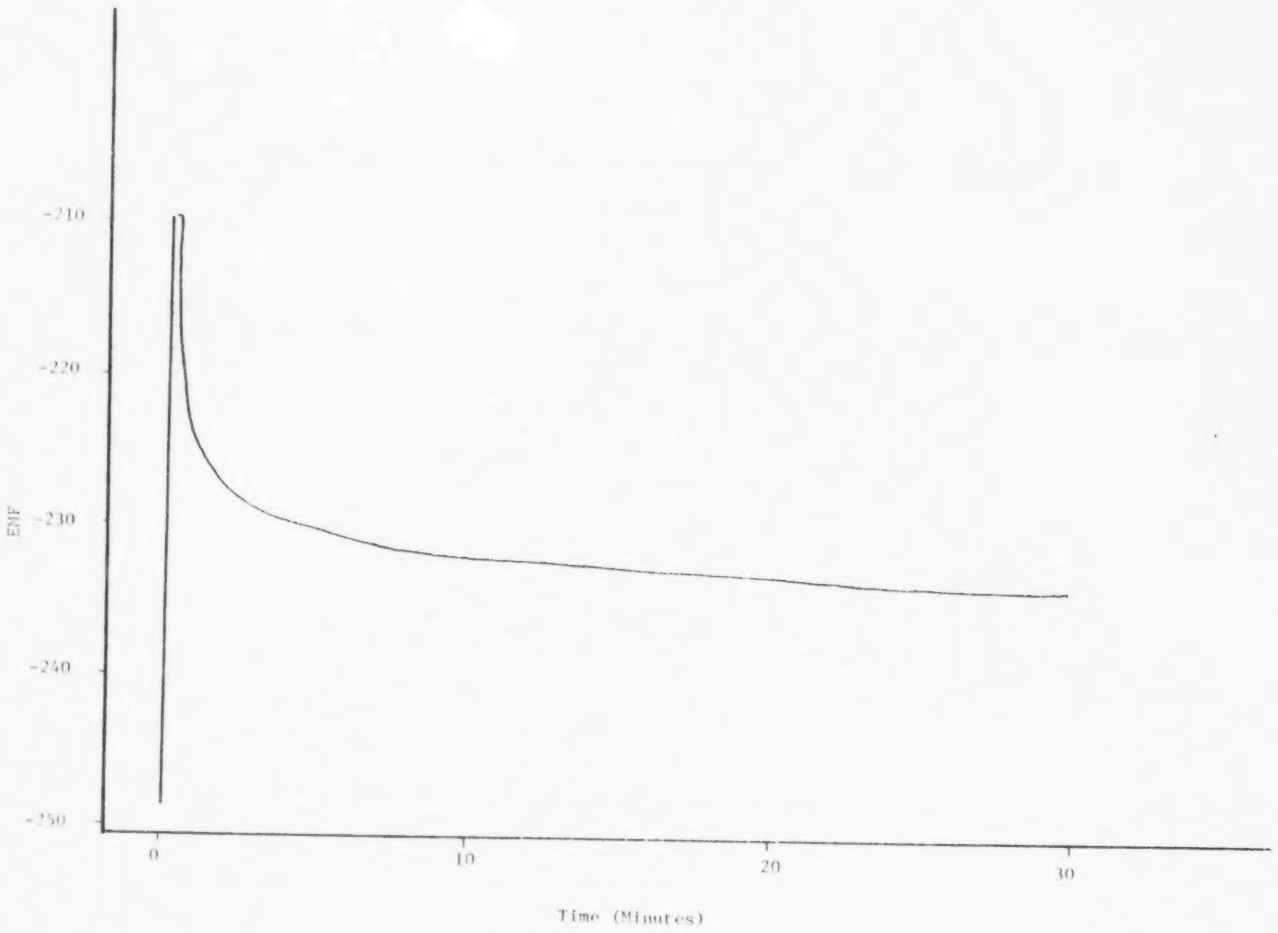

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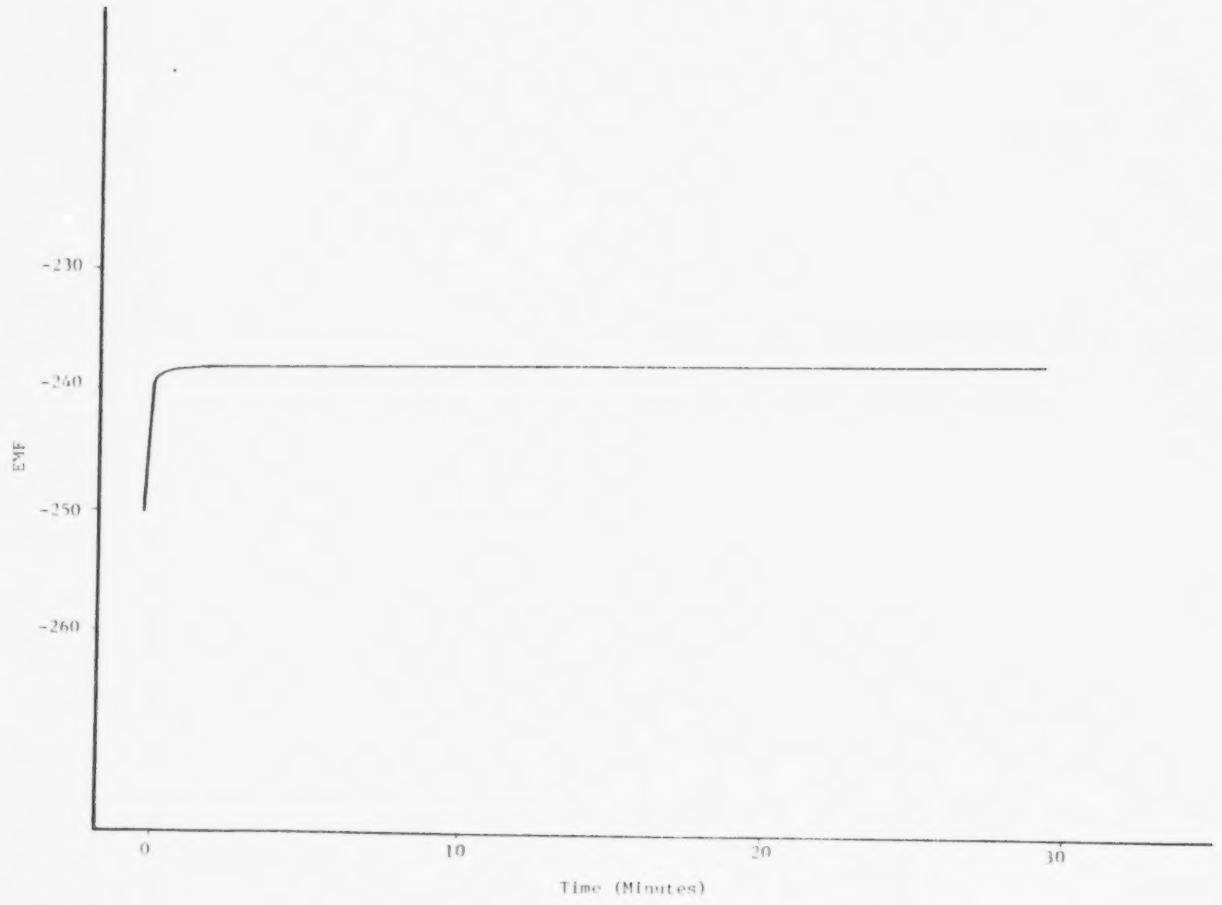
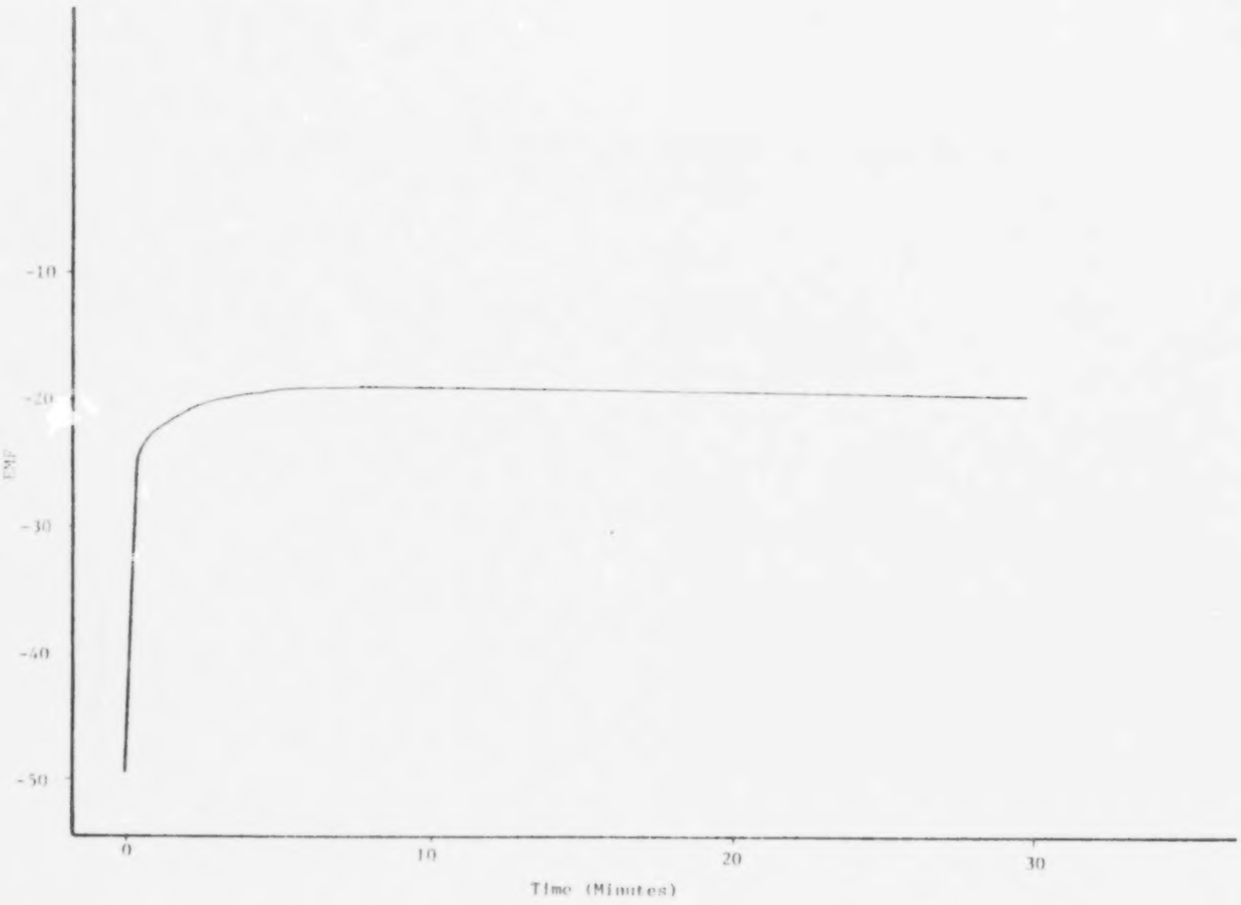


PLANT BOWEN

DIVALENT CATION SPECIFIC ION ELECTRODE - RUN NO. 5



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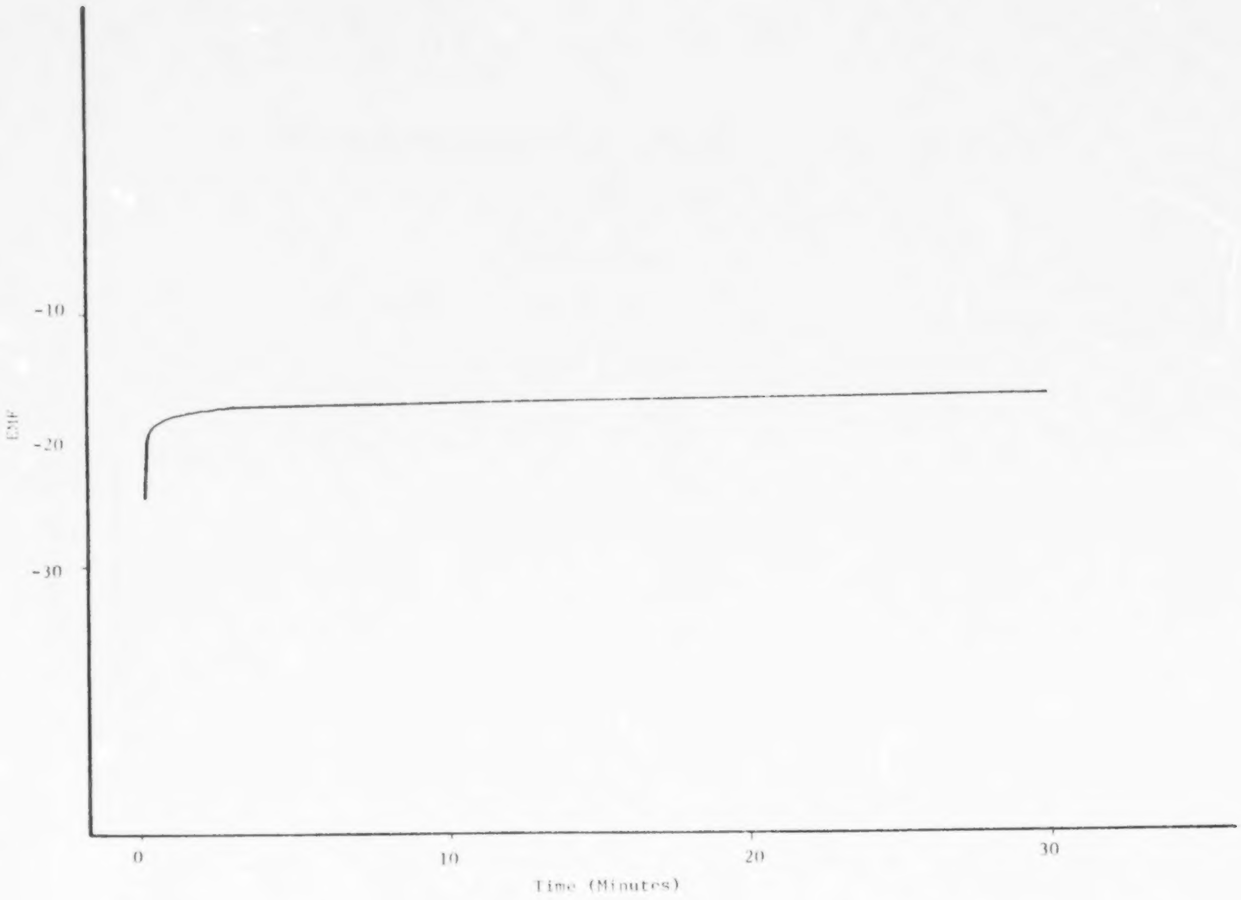

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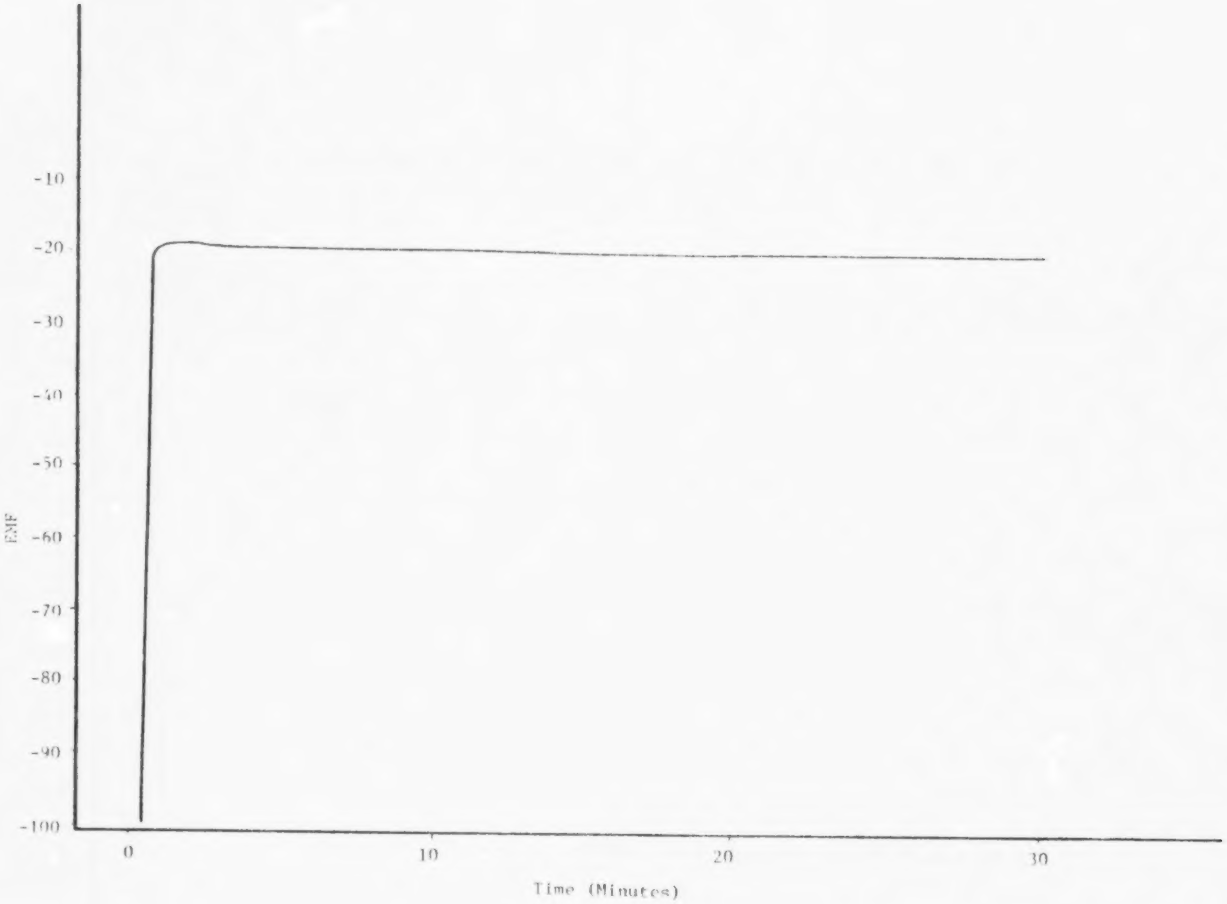

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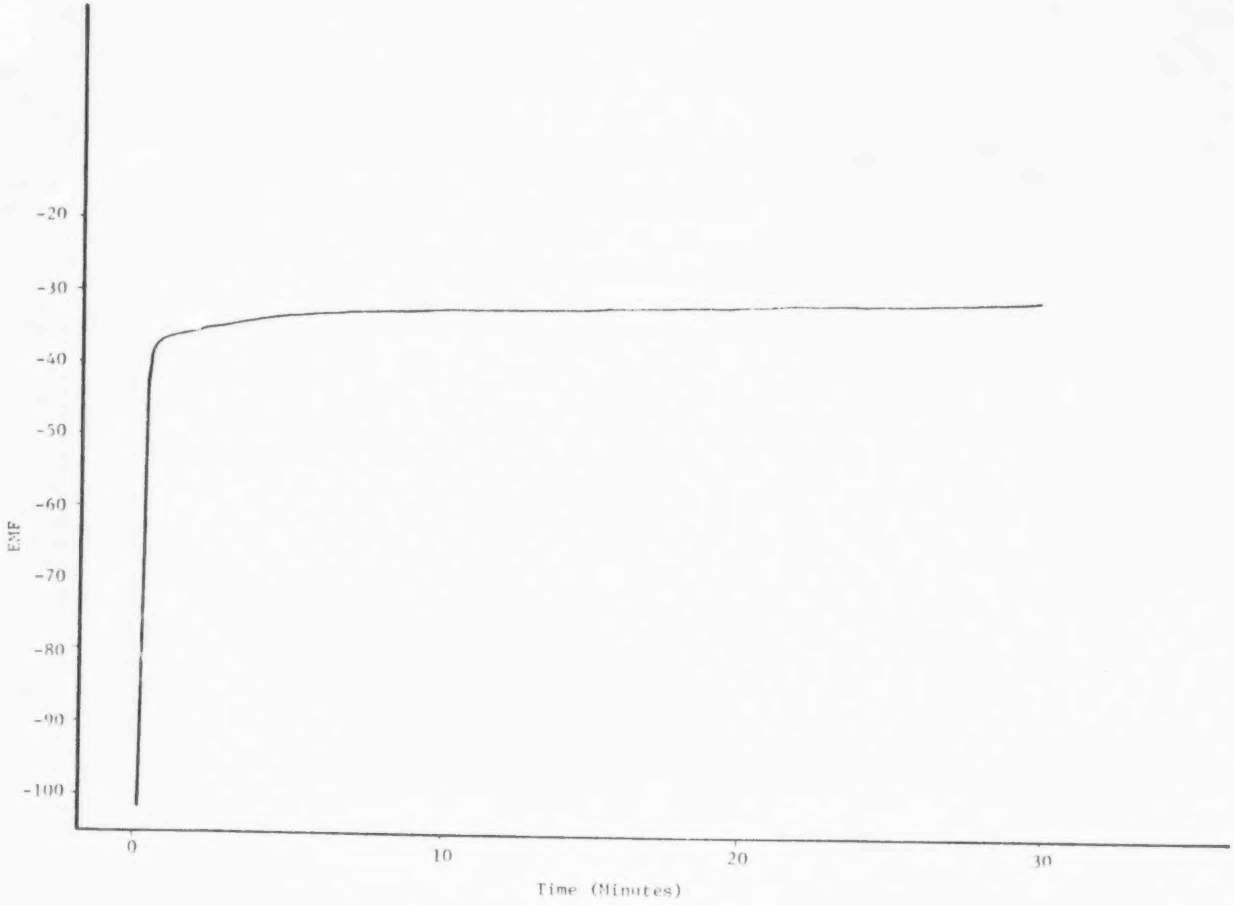

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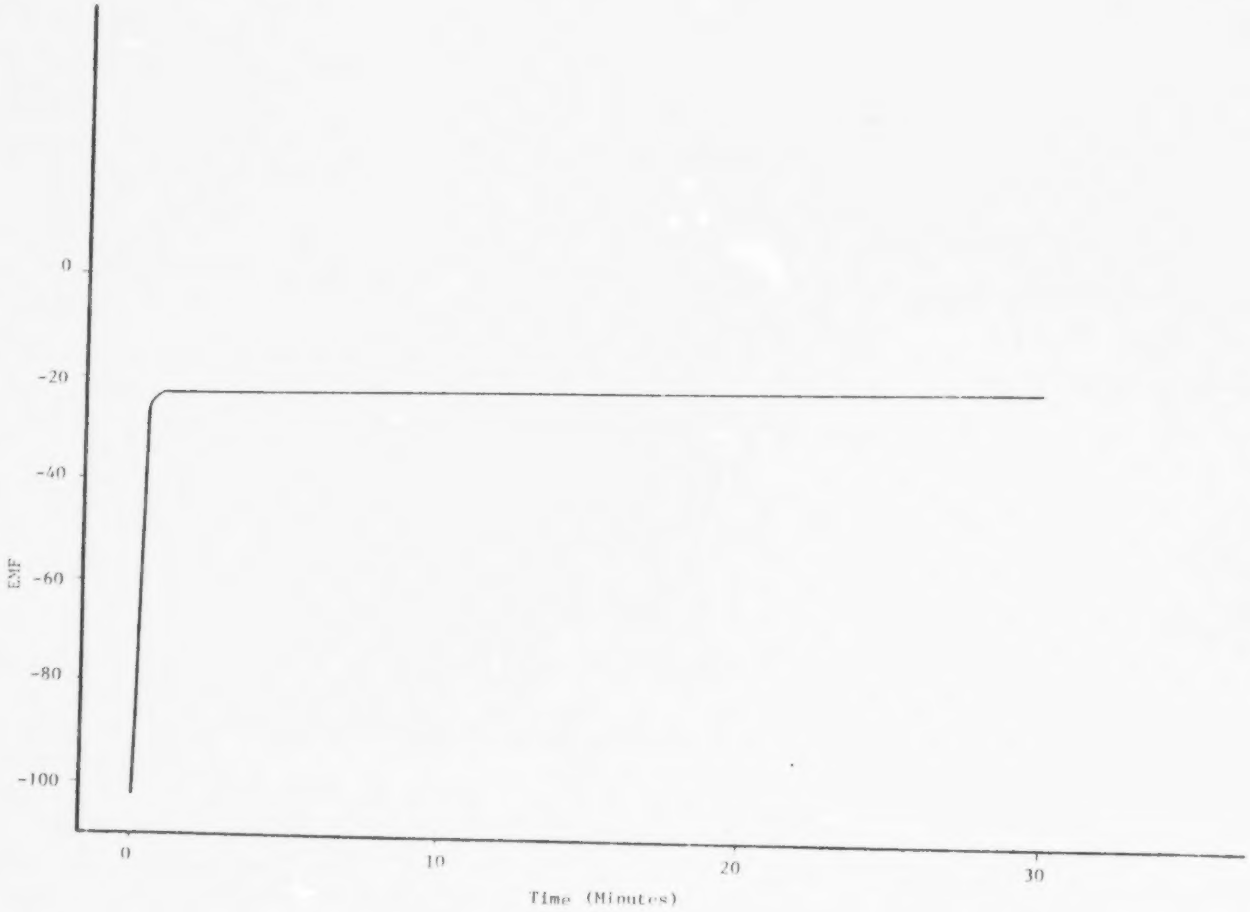
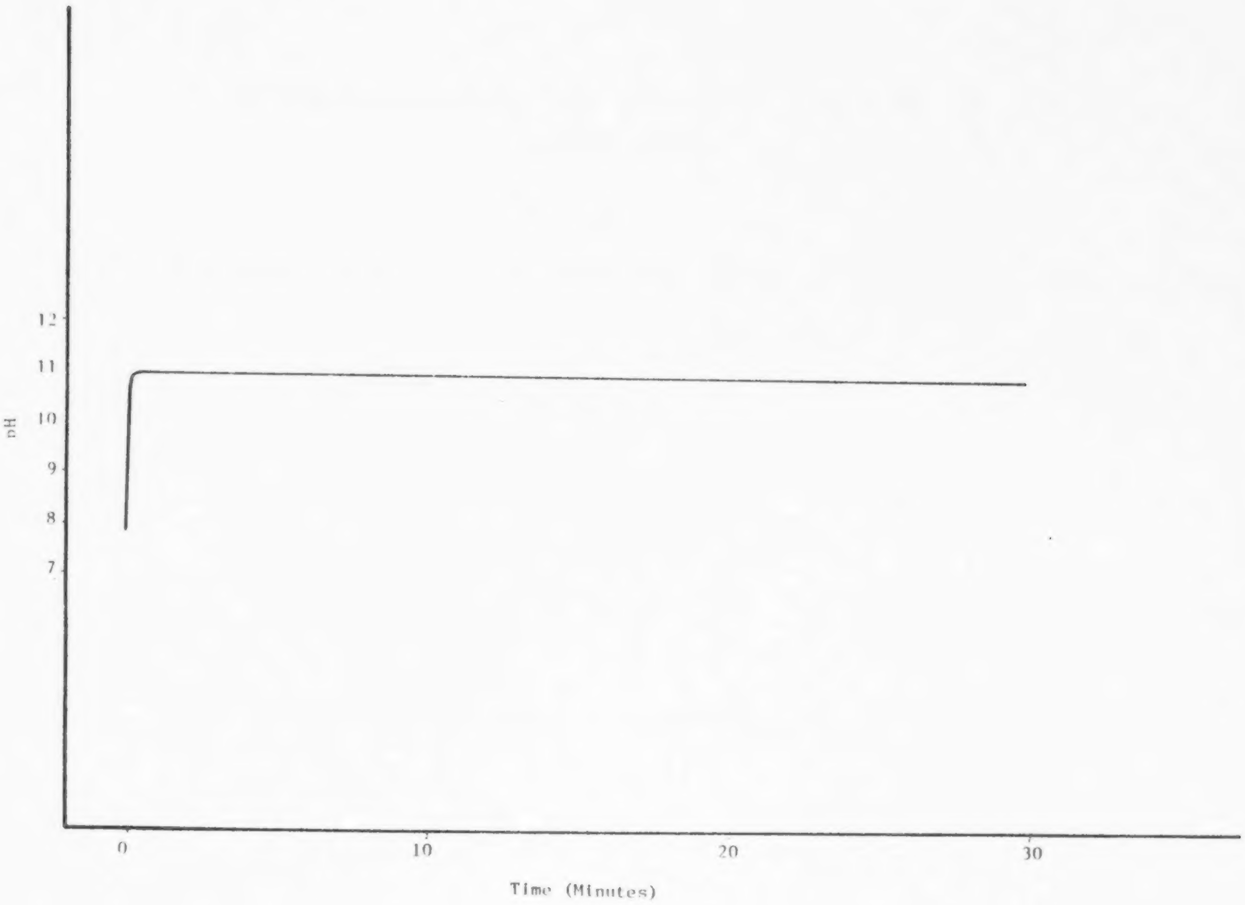
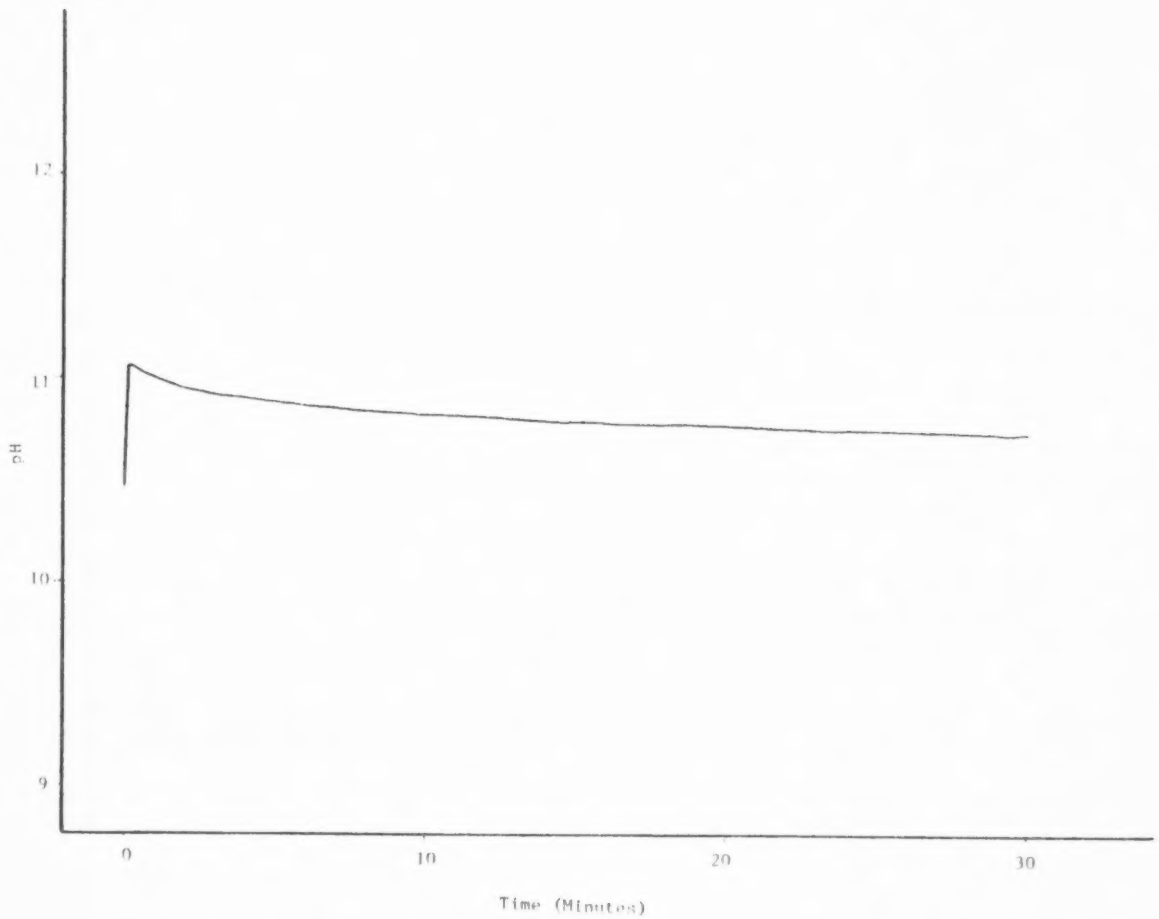


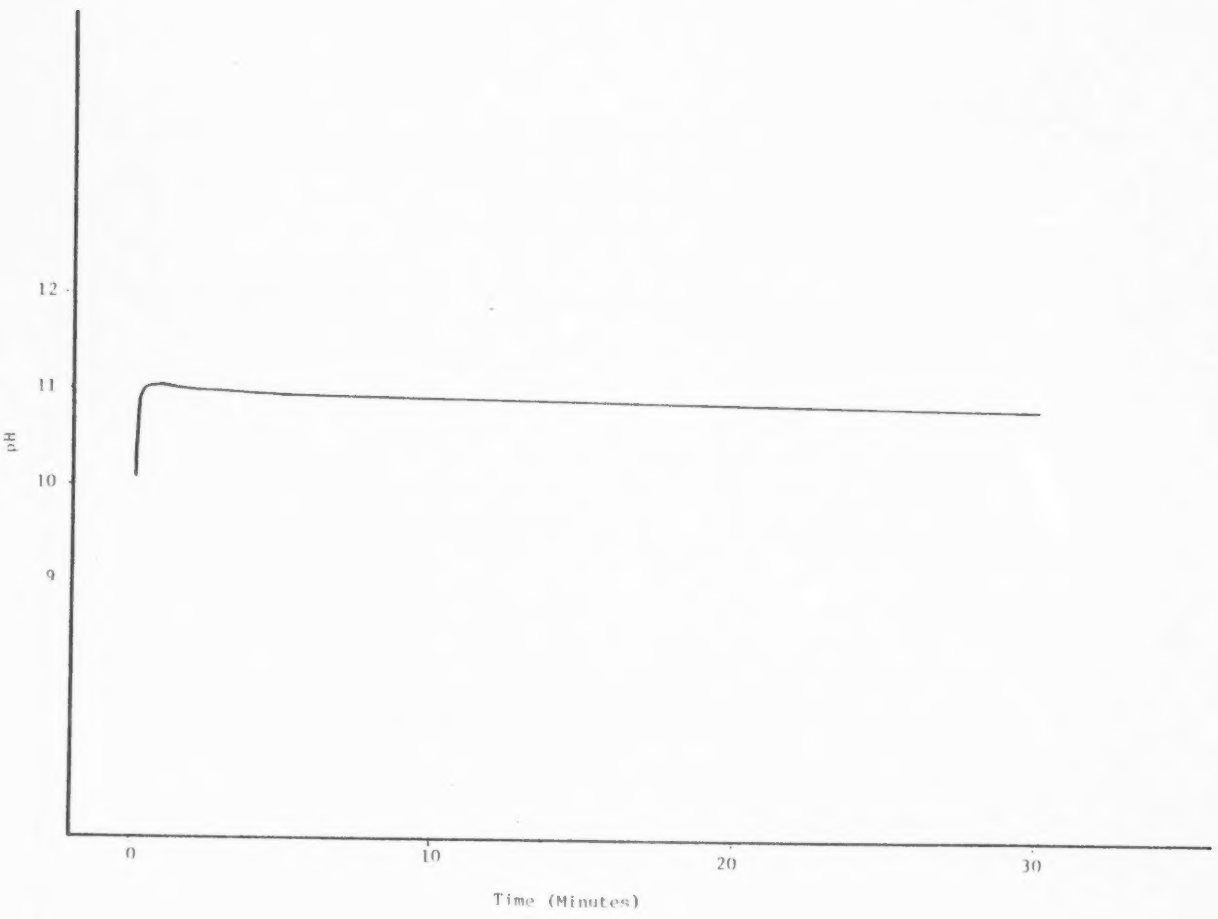
PLANT BOWEN
CALCIUM SPECIFIC ION ELECTRODE - RUN NO. 5



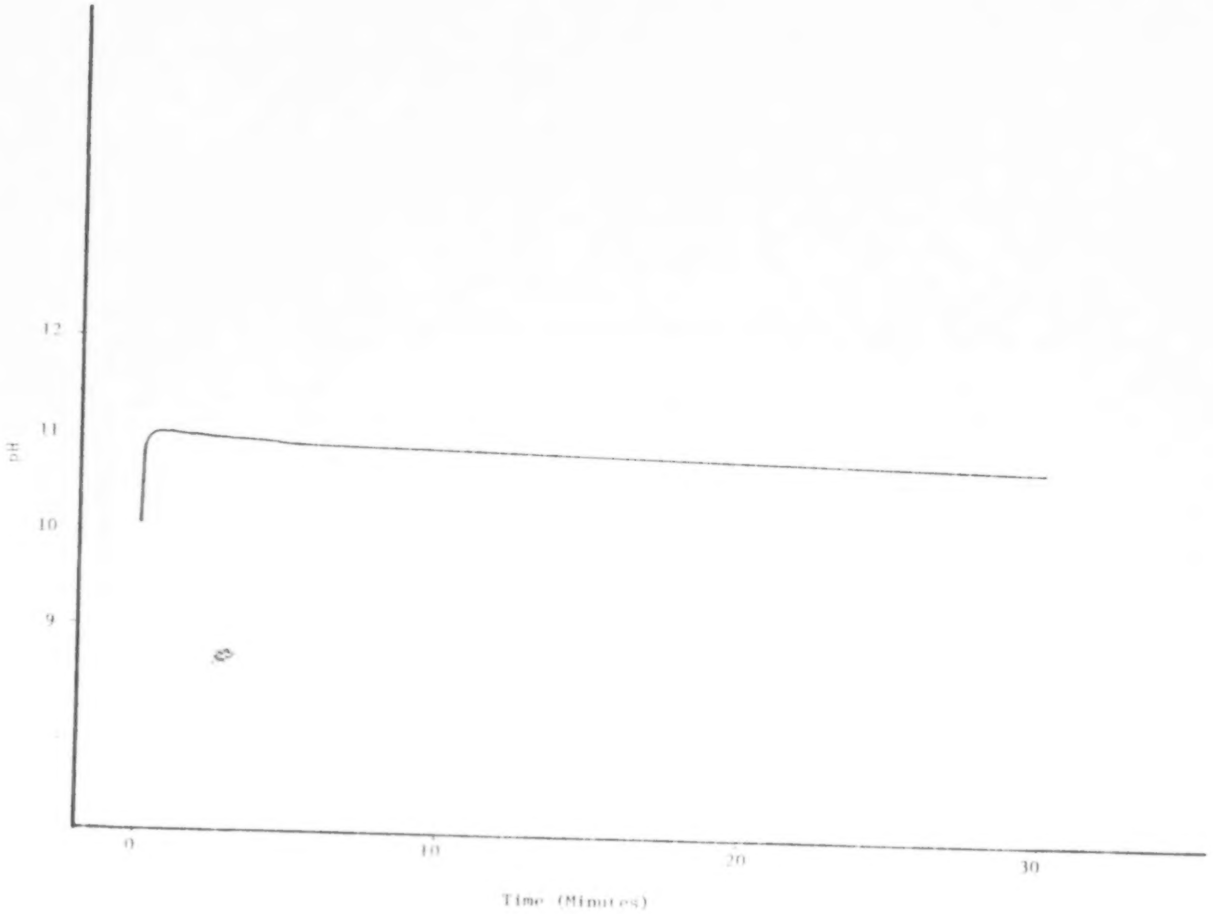
PLANT BOWEN
pH - RUN NO. 1



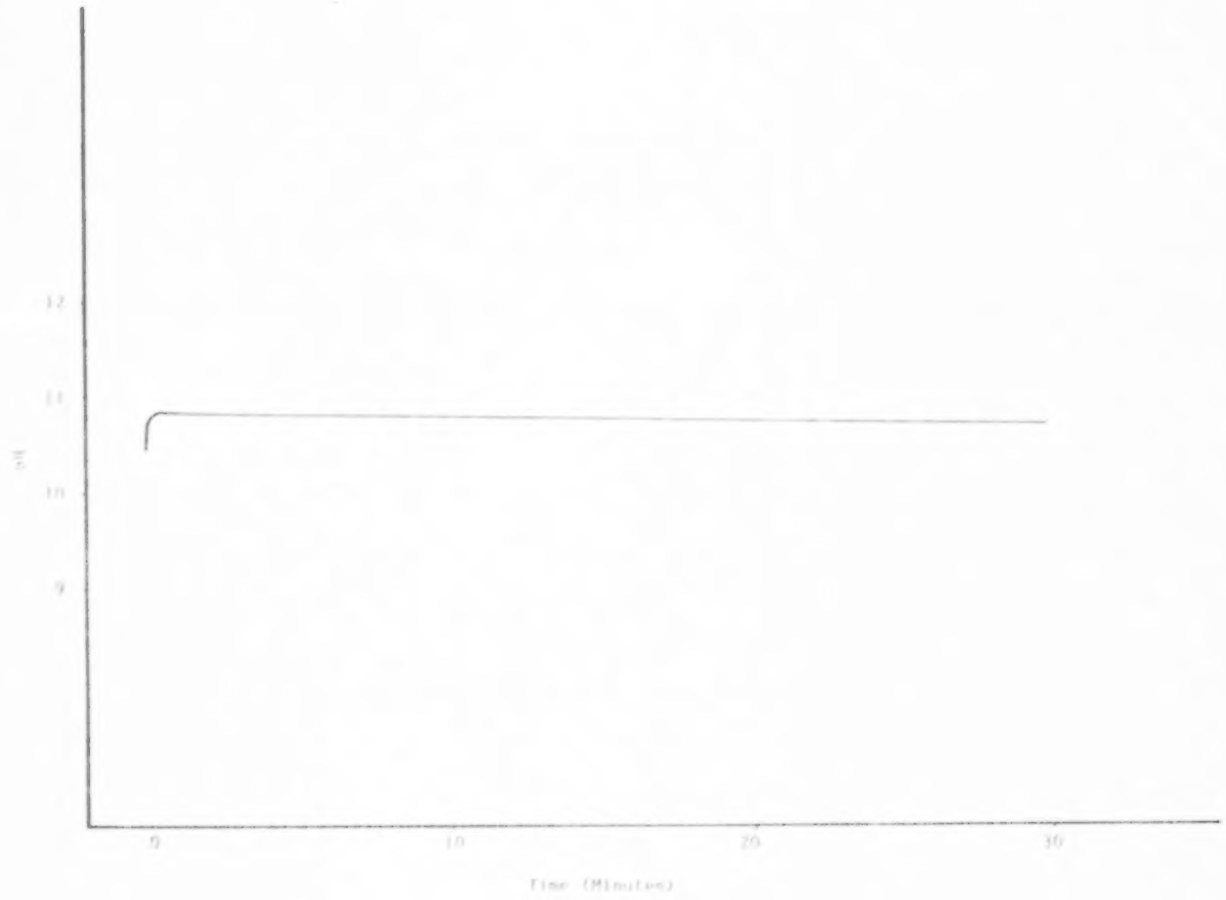
PLANT BOWEN
pH - RUN NO. 2



PLANT BOWEN
pH - RUN NO. 3



PLANT BOWEN
pH - RUN NO. 4



PLANT BOWEN
pH - RUN NO. 5

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